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CXXXV.—*The Constituents of Hops.*

By FREDERICK BELDING POWER, FRANK TUTIN, and
HAROLD ROGERSON.

ON account of the extended use of hops in the brewing industry, and also, but in a very much less degree, for medicinal purposes, they have been the subject of numerous investigations. The chief object of these investigations appears to have been to ascertain the nature of the bitter principles, or to determine the proportion in which they are present. Although a considerable number of products have thus from time to time been obtained, to which various names and formulæ have been assigned, the character of most of them clearly indicates that they do not represent definite chemical compounds. Apart from the essential oil yielded by the distillation of hops with steam, which has been the subject of several independent investigations by Chapman and others (T., 1903, **83**, 505; *J. pr. Chem.*, 1911, [ii], **83**, 483), the determination of the presence of tannin and sugar, and the isolation of a very small amount of choline, the information respecting the other constituents, which are mostly contained in the resinous material, has been exceedingly deficient and by no means satisfactory. The confusion which pervades the subject will be apparent from the following brief survey of the literature.

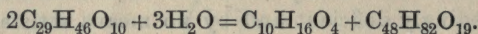
Vlaanderen (*Jahresb. Chem.*, 1858, p. 448) obtained from lupulin (the glandular powder from hops) a resin to which he assigned the formula $C_{54}H_{70}O_{11}$, and from which copper compounds of varying composition were prepared.

Wagner (*Dingler's polyt. J.*, 1859, **154**, 65), in determining the tannin of hops, states that he found a yellow colouring matter which behaved towards reagents like quercitrin, and could be split into quercetin and dextrose, but no evidence of the identity of these substances was recorded. The tannin ("humulotannic acid") has been especially studied by Etti (*Annalen*, 1876, **180**, 223), and more recently by Chapman (*J. Inst. Brewing*, 1907, **13**, 646), with reference to its quantitative determination.

Lermer (*J. pr. Chem.*, 1863, **90**, 254) states to have isolated from hops a crystalline substance, insoluble in water, but the alcoholic solution of which possessed a bitter taste. This substance, which was very unstable, becoming in a few hours soft and yellow, was called the bitter acid of hops ("hopfenbittersäure"), and from the analysis of a copper compound it was considered to possess the formula $C_{32}H_{50}O_7$. Lermer also indicated that the hop gland contains a wax consisting of myricyl palmitate.

H. Bungener (*Bull. Soc. chim.*, 1886, [ii], **45**, 487) confirmed the observation of Lermier (*loc. cit.*) respecting the occurrence of a crystalline acid, insoluble in water, which rapidly became yellow and resinous on exposure to the air. He designated the substance "lupulic acid," stating it to melt at 92–93°, and to agree in composition with the formula $C_{50}H_{70}O_8$. It was furthermore considered that it is the resinous oxidation product of this acid which imparts bitterness to a decoction of hops, and that this resinous product exists in hops together with the acid from which it is readily formed. Bungener and Fries (*Zeitsch. ges. Brauw.*, 1885, **8**, 267) have stated that hops contain asparagine, but although the method of separation was given, no analysis or other evidence of the identity of the substance appears to have been recorded.

Issléib (*Arch. Pharm.*, 1880, **13**, 345), from the results of a somewhat extended investigation, has concluded that hops contain a peculiar bitter substance, "hop-bitter," of the composition $C_{29}H_{46}O_{10}$. This, when treated with dilute sulphuric acid, is said to be converted into a resinous product, "lupuliretin," $C_{10}H_{16}O_4$, and a crystalline, bitter substance, "lupulinic acid," $C_{48}H_{82}O_{19}$, which is insoluble in water, the change being represented by the following equation:



The same author, furthermore, assigns to hop-resin the formula $C_{10}H_{14}O_3$, and assumes that by the simple addition of a molecule of water it is converted into "lupuliretin," $C_{10}H_{16}O_4$. On the other hand, hop-resin, $C_{10}H_{14}O_3$, is considered to be produced by the oxidation of the essential oil of hops, the latter being given the formula $C_{10}H_{18}O$, and the change represented as follows: $C_{10}H_{18}O + 2O_2 = C_{10}H_{14}O_3 + 2H_2O$. Inasmuch as it is well known, however, that both hop-resin and the essential oil of hops are very complex products, the latter consisting largely of a sesquiterpene, $C_{15}H_{24}$, the fallacy of the above conclusions is apparent.

Hayduck (*Woch. Brau.*, 1887, **4**, 397; 1888, **5**, 937) has differentiated three resinous constituents of hops as follows: α -resin, which is soft, soluble in light petroleum, and precipitable by an alcoholic solution of lead acetate; β -resin, which is similar to the preceding, but is not precipitable by lead acetate; and γ -resin, which is a hard solid, insoluble in light petroleum, but soluble in ether or alcohol, and not precipitable by lead acetate. The solutions of both the α -resin and the β -resin were said to be intensely and disagreeably bitter.

Lintner and A. Bungener (*Zeitsch. ges. Brauw.*, 1891, **14**, 357) note that in the α -resin of Hayduck (*loc. cit.*) crystals were formed after some time which appeared to be different from H. Bungener's hop-

bitter acid (*loc. cit.*). They obtained a crystalline product, melting at 56° , which showed but little tendency to resinify, and this was supposed to be identical with the bitter substance of Lerner. Seyffert and von Antropoff (*Zeitsch. ges. Brauw.*, 1896, **19**, 1), in an attempt to compare the products obtained by them with those of other investigators, were led to conclude that hop resins are mixtures of substances in a state of progressive decomposition.

Barth (*Zeitsch. ges. Brauw.*, 1900, **23**, 509, 537, 554, 572, 594), who has reviewed the results of earlier investigators, states that the formula of lupulic acid is not $C_{50}H_{70}O_8$, as given by H. Bungener (*loc. cit.*), but $C_{25}H_{36}O_4$, and that there is no doubt of its identity with Lerner's bitter acid. On oxidation with permanganate, it gave valeric acid. He also indicates that the so-called lupulic acid does not contain a carboxyl group, since it can be recovered from an alkaline solution by extraction with ether. On the other hand, it is stated that when fused with potassium hydroxide, it yields a hydrocarbon having a density of 0.8840 at 15° , the composition of which is most simply expressed by the formula C_5H_8 . From this result it was considered that lupulic acid is a derivative of an olefinic terpene. The author, furthermore, notes the points of distinction between α -lupulic acid (m. p. $54-56^{\circ}$), which was observed by Hayduck to be a constituent of the so-called α -resin, and is said to crystallise in small rhombohedra, and β -lupulic acid (m. p. 92°), which has been described as forming long, glistening prisms. Both compounds were presumed to be unsaturated, to possess similar molecular weights, and to stand in some relationship to the essential oil of hops.

Bamberger and Landsiedl (*Zeitsch. ges. Brauw.*, 1902, **25**, 461) describe the α -lupulic acid or hop-bitter acid as an amber-coloured, crystalline mass (m. p. 56°), which is readily soluble in nearly all solvents, and when oxidised by exposure to the air gives with ferric chloride a yellowish-brown coloration. They considered it to possess the formula $C_{20}H_{28}O_5$ or $C_{20}H_{30}O_5$.

Lintner and Schnell (*Zeitsch. ges. Brauw.*, 1904, **27**, 666) were not successful in their attempts to obtain α -lupulic acid in a pure state, and they therefore examined the products formed from the acid by the action of an alcoholic solution of sodium hydroxide. They thus obtained, besides resinous matter and valeric acid, a crystalline substance (m. p. 92.5°), which was considered to possess the formula $C_{15}H_{24}O_4$, and to be an unsaturated hydroxyketonic acid. They also proposed to designate the above-mentioned α -acid as "humulon," and its crystalline product of decomposition as "humulin," retaining for the so-called β -acid the name "lupulic acid."

Siller (*Zeitsch. Nahr. Genussm.*, 1909, **18**, 241), with consideration of the investigation of Hayduck (*loc. cit.*), has proposed a method for quantitatively determining the α -, β -, and γ -resins of the last-mentioned author, and also the so-called α -hop-bitter acid. Since the latter substance was obtained from the lead compound of the mixed resins by decomposing it with sulphuric acid, it must have consisted to a large extent of ordinary fatty acids, which the present authors have shown to be contained in considerable amount in hops.

Adler (*Zeitsch. ges. Brauw.*, 1912, **35**, 406) and Seibriger (*Woch. Brau.*, 1913, **30**, 177, 196) have suggested methods for determining the bitter substances of hops by extracting the latter with light petroleum or carbon tetrachloride, and titrating the resulting extract with alcoholic potassium hydroxide. Such methods, however, are entirely empirical, and, as in the case of the method proposed by Siller (*loc. cit.*), the substances actually determined would no doubt consist chiefly of fatty acids.

Griessmayer (*Dingler's polyt. J.*, 1874, **212**, 67) distilled a decoction of hops with an alkali hydroxide, and obtained, besides ammonia and trimethylamine, a small amount of a liquid which was said to have an odour resembling that of coniine. This very indefinite substance was presumed to be a volatile alkaloid, for which the name "lupuline" was proposed, but no crystalline salt could be prepared from it, nor does the presence of nitrogen appear to have been determined.

Griess and Harrow (*Ber.*, 1885, **18**, 717) showed that hops contain a very small proportion (not more than 0.02 per cent.) of choline. As a very dilute solution of choline was found to dissolve relatively large amounts of hop-resin, whereby an intensely bitter taste was imparted to the liquid, they thought it not unlikely that such a combination occurs in the hops, thus forming the bitter substance which is soluble in water.

The preceding survey of the very voluminous literature pertaining to the chemistry of hops, although by no means complete, will afford an indication of the present state of knowledge on the subject. In view of the existing confusion, it has been considered that other and more systematic methods of examination than those hitherto employed might serve more clearly to define the character of the constituents of this important natural product, and thus explain the numerous discrepancies of statement. The results of the present investigation, with the deductions from them, are summarised at the end of this paper.

EXPERIMENTAL.

The material used in this investigation consisted of a good quality of fresh Kentish hops, from the crop of 1911.

A small portion (10 grams) of the material was subjected to a preliminary test for an alkaloid, when indications were obtained of the presence of a very small amount of such a substance.

In order to ascertain whether an enzyme were present, 200 grams of the ground material were macerated with water at the ordinary temperature. To the expressed and filtered liquid about twice its volume of alcohol was added, but the precipitate thus produced was quite insignificant.

Determinations of the moisture and ash, with the use of air-dried material, gave the following results:

0.5762 of hops, on heating at 110° , lost 0.0604 H_2O . $\text{H}_2\text{O}=10.48$ per cent.

10.0 of hops gave, on incineration, 0.7919 of ash. Ash=7.919 per cent.

The amount of tannin present was determined by Chapman's method (*J. Inst. Brewing*, 1907, **13**, 646) with the following results:

Two portions of infusion, each representing 1 gram of hops, gave 0.0400 and 0.0402 respectively of cinchonine tannate. The corresponding amounts of tannin are thus equivalent to 2.40 and 2.41 per cent. respectively of the weight of the hops.

A portion (25 grams) of the ground hops was completely extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100° , were obtained:

Petroleum (b. p. $35-50^{\circ}$)	extracted	5.45 grams	=	21.80	per cent.
Ether	"	0.65	"	2.60	" "
Chloroform	"	0.80	"	2.40	" "
Alcohol	"	2.15	"	8.60	" "
Total.....		8.85 grams		35.40	per cent.

For the purpose of a complete examination, 25 kilograms of the ground material were completely extracted with hot alcohol, when, after the removal of the greater part of the solvent, 9.1 kilograms of a viscid, dark green extract were obtained.

Distillation of the Extract with Steam and Separation of the Essential Oil.

The entire amount of the above-mentioned extract was mixed with water, and the mixture distilled in a current of steam. On extracting the distillate with ether, and removing the solvent, a quantity of a pale yellow, essential oil was obtained. This oil

naturally differed considerably in its characters from that obtained by the direct distillation of hops with steam, and, with consideration of the fact that it is not a normal product, it has not been deemed desirable to record its constants.

Non-volatile Constituents of the Extract.

After the removal of the essential oil, as above described, there remained in the distillation flask a dark-coloured aqueous liquid (A) and a dark green, oily resin (B). The resin was separated, and, in order to wash it, thoroughly mixed with boiling water, when an emulsion was formed. The latter was shaken with light petroleum, after which the aqueous layer, which contained suspended resin, was filtered, the filtrate being concentrated and added to the main portion of the aqueous liquid. The petroleum liquid was then evaporated, and the residue mixed with the solid which had been collected on the filter, the total amount of resin being thus brought together.

Examination of the Aqueous Liquid (A).

A portion of the aqueous liquid, representing 2 kilograms of the original extract, was first thoroughly extracted with ether and then with chloroform. These solvents removed some brown, viscid material, amounting to about 12 and 3 grams respectively. Both of these products possessed a very bitter taste, and gave a brown coloration with ferric chloride. Their respective solutions in ether and chloroform were shaken with dilute aqueous hydrogen chloride, but the acid liquids afforded no definite indications of the presence of an alkaloid. On subsequently extracting the ethereal and chloroform liquids with aqueous alkalis, only dark-coloured, amorphous products were obtained.

The aqueous liquid which had been extracted with both ether and chloroform was next shaken with several successive portions of amyl alcohol. This treatment removed a quantity (about 29 grams) of a dark brown, viscid product, which possessed an acrid taste and yielded, in aqueous solution, a green colour with ferric chloride. Separate portions of it were heated with dilute sulphuric acid and aqueous potassium hydroxide respectively, but nothing definite could be obtained by this treatment.

After extracting the aqueous liquid with amyl alcohol, as above described, it was concentrated somewhat under diminished pressure and then treated with a slight excess of basic lead acetate solution, when a brown precipitate was produced. The latter was collected, washed, suspended in water, decomposed by hydrogen sulphide, and the liquid filtered. The filtrate, on concentration under diminished

pressure, yielded a dark-coloured product which appeared to consist only of tannin and amorphous colouring matter. This conclusion was confirmed by heating a portion of the liquid with potassium hydroxide, acidifying, extracting with ether, and shaking the ethereal liquid with aqueous ammonium carbonate. A small amount of substance was thus obtained, which evidently consisted of gallic acid, and had been formed from the tannin originally present. On methylation, it yielded trimethylgallic acid, melting at 164° .

The filtrate from the precipitate produced by basic lead acetate was deprived of lead by means of hydrogen sulphide, filtered, and concentrated to the consistency of a syrup. The latter evidently contained a large quantity of sugar, since it readily yielded *d*-phenylglucosazone (m. p. $208-209^{\circ}$), but it gave nothing crystalline on acetylation. When diluted with alcohol, and kept for some time, it deposited a quantity (about 5.5 grams) of potassium nitrate.

Isolation of Choline, $C_5H_{15}O_2N$.

The occurrence of choline in hops was conclusively shown some years ago by Griess and Harrow (*Ber.*, 1885, **18**, 717), but for the purpose of completeness it was deemed desirable to determine its presence in the material under investigation. The above-mentioned liquid, from which the potassium nitrate had been removed, was therefore concentrated under diminished pressure, the syrupy liquid thoroughly extracted with alcohol, and the resulting liquid evaporated. The residue from the latter was repeatedly treated with alcohol in the same manner until a product was finally obtained which was soluble in nearly absolute alcohol. To the alcoholic solution thus obtained, a little hydrochloric acid was added, and subsequently an alcoholic solution of mercuric chloride, the mixture being then kept for some time. The precipitate which had formed was collected, dissolved as completely as possible in warm water, and the mercury removed from the solution by means of hydrogen sulphide, after which the filtered liquid was nearly neutralised with sodium carbonate and evaporated to dryness under diminished pressure. The product was then treated with absolute alcohol, the filtered liquid concentrated, and this operation repeated until the inorganic salt was completely eliminated. On the addition of platinic chloride to the final alcoholic solution, an orange-coloured precipitate was produced. The latter was collected, washed with absolute alcohol, and dried on a porous plate, when it melted and decomposed at $233-238^{\circ}$:

0.0304, dried at 110° , gave 0.0098 Pt. Pt = 32.2.

$(C_5H_{14}ONCl)_2PtCl_4$ requires Pt = 31.7 per cent.

Isolation of l-Asparagine, C₄H₈O₃N₂.

Although it has been stated by Bungener and Fries (*Zeitsch. ges. Brauw.*, 1885, **8**, 267), that hops contain asparagine, they appear to have recorded no analysis or other evidence of the identity of the substance isolated, and it therefore seemed desirable to confirm its presence.

An amount of the original aqueous liquid (A), representing one kilogram of the alcoholic extract of the hops, was treated with a slight excess of barium hydroxide, and the excess of alkali then removed by means of carbon dioxide. To the filtered liquid a slight excess of a solution of basic lead acetate was added, and the filtrate from the precipitate thus produced then slightly acidified with acetic acid. On the subsequent addition of an aqueous solution of mercuric nitrate, prepared with the aid of just sufficient nitric acid to dissolve the salt, a considerable amount of a nearly white precipitate was produced. This was collected, washed, suspended in water, and decomposed with hydrogen sulphide, after which the filtered liquid was neutralised with ammonia, then slightly acidified with acetic acid, and concentrated under diminished pressure. On keeping the resulting syrup, a quantity (4.2 grams) of a substance separated in large, colourless prisms, which were recrystallised from water:

0.1972* gave 0.2635 CO₂ and 0.1095 H₂O. C=36.4; H=6.2.

C₄H₈O₃N₂ requires C=36.4; H=6.1 per cent.

This substance was lævorotatory in aqueous solution, and was thus evidently *l*-asparagine. The amount obtained was equivalent to about 0.015 per cent. of the weight of hops employed.

Examination for a Volatile Alkaloid.

It was noted many years ago by Griessmayer (*Dingler's polyt. J.*, 1874, **212**, 67) that hops contain a very small amount of a volatile base, which possesses an odour resembling that of coniine, and it was therefore sought to confirm this statement.

A quantity of the aqueous liquid (A), representing 4 kilograms of the original alcoholic extract of the hops, was concentrated, rendered alkaline with potassium hydroxide, and distilled in a current of steam for four hours. The distillate was then extracted with ether, the ethereal liquid being subsequently shaken with dilute hydrochloric acid. This aqueous acid liquid was made alkaline with potassium hydroxide, extracted with ether, and the ethereal liquid evaporated, when a small residue, having a strong,

* Dried at 130°.

coniine-like odour, was obtained. The residue was dissolved in a small amount of dilute alcohol, acidified by the addition of a few drops of decinormal hydrochloric acid, the liquid filtered, and evaporated to dryness in a vacuum desiccator. A very small, varnish-like residue was thus obtained, which, when dissolved in water, gave decided reactions with the usual alkaloid reagents, and when made alkaline developed an odour recalling that of coniine. This result served to confirm the observation of Griessmayer (*loc. cit.*) respecting the occurrence in hops of a volatile alkaloid, but the amount present is so extremely small that it has not been possible further to characterise it.

Examination of the Resin (B).

The crude, resinous material which had been separated from the aqueous liquid (A), as previously described, was mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a large Soxhlet apparatus with various solvents. The weights of the products, as determined by evaporating aliquot portions of the respective extracts and drying the residues at 100°, were as follows:

Petroleum (b.p. 35—50°)	extracted	2635	grams.
Ether	" "	692	"
Chloroform	" "	66	"
Ethyl acetate	" "	30	"
Alcohol	" "	104	"
Total... ..		3527	grams

The above amount of resin is equivalent to about 14·1 per cent. of the weight of hops employed.

Petroleum Extract of the Resin.

This extract, after the complete removal of the solvent, formed a dark green, viscid mass. A quantity (750 grams) of the extract was introduced into a distillation flask, some water added, and steam passed through the mixture for five hours. By this means a small amount of essential oil was eliminated which had not been removed by the distillation of the original alcoholic extract with steam. The contents of the distillation flask were then shaken with a large volume of ether, and the ethereal layer, which contained a relatively small amount of a sparingly soluble solid in suspension, was filtered, the solid being well washed with ether. This solid was a neutral, wax-like substance, and could not be obtained free from chlorophyll by crystallisation. It was therefore heated with alcoholic potassium hydroxide, when it yielded ceryl alcohol (m. p. 78°) and cerotic acid (m. p. 79°), and thus appears

to have consisted of ceryl cerotate. Larger amounts of both the respective alcohol and acid were subsequently obtained. The ethereal filtrate and washings from the wax, which were free from alkaloid, appeared to contain chiefly fatty matter and chlorophyll, together with some free fatty acids. As it was not deemed necessary to examine the free and combined fatty acids separately, the ether was removed, the residue dissolved in alcohol, and hydrolysed by boiling for two hours with potassium hydroxide, when during the operation ammonia was evolved. The alcohol was then removed, water added, and steam passed through the mixture for some time. By this treatment the last remaining portions of essential oil occluded by the fatty material were eliminated, and, on examination, were found to consist chiefly of sesquiterpene.

The alkaline, aqueous liquid which had been distilled with steam, as above described, was extracted many times with ether for the removal of the unsaponifiable material. During this operation an emulsion formed in the lower portion of the ethereal layer, and this, when collected and well washed with ether, yielded a soap-like solid, which was found to consist of potassium cerotate.

Examination of the Unsaponifiable Material.

The ethereal liquid obtained by extracting the hydrolysed petroleum extract of the resin with ether, as above described, was dried, and the solvent removed. A viscid, dark yellowish-brown product was thus obtained, which amounted to about 140 grams.

Isolation of Ceryl Alcohol and Hentriacontane.

The above-mentioned, dark yellowish-brown product was dissolved in about 700 c.c. of hot alcohol, when, on cooling, a solid separated and was collected. This solid, which was obviously a mixture, was dissolved in pyridine, and heated for a short time with an excess of phthalic anhydride. Water was then gradually added to the warm liquid, and the mixture extracted with ether, the ethereal liquid being freed from pyridine by means of dilute sulphuric acid, and then shaken with aqueous sodium carbonate. During the latter operation a quantity of a solid sodium salt of an acid phthalic ester separated, and was collected. The latter was hydrolysed with alcoholic potassium hydroxide, after which the alcohol was removed, water added, and the mixture extracted with ether. A quantity of a solid was thus obtained which, when crystallised from alcohol, separated in colourless, glistening leaflets, melting at 78—79°. This substance, which amounted to 5 grams, was identified as ceryl alcohol (Found, C=81.7; H=14.0. Calc., C=81.8; H=14.1 per cent.).

The ethereal liquid from which the sodium salt of the acid phthalic ester of ceryl alcohol had been separated, as above described, was dried and evaporated, when a solid (about 3 grams) of low melting point was obtained. The latter was crystallised from ethyl acetate, when it formed nacreous leaflets, melting sharply at 68° , and was identified as hentriacontane (Found, $C=84.8$; $H=14.9$. Calc., $C=85.3$; $H=14.7$ per cent.).

Isolation of a Phytosterol, $C_{27}H_{46}O$.

The original alcoholic mother liquors from the mixture of ceryl alcohol and hentriacontane were diluted somewhat with water, and kept for some time, when, although the greater part of the material separated as a brown, viscid product, a substance in the form of crystalline plates was slowly deposited. The latter substance, which gave the colour reaction of the phytosterols, was collected, and crystallised several times from a mixture of ethyl acetate and dilute alcohol. It then separated in large, colourless leaflets, melting at $135-136^{\circ}$, and amounted to about 2 grams:

0.1164, on heating at 110° , lost 0.0054 H_2O . $H_2O=4.6$.

0.1110 * gave 0.3402 CO_2 and 0.1194 H_2O . $C=83.6$; $H=12.0$.

$C_{27}H_{46}O, H_2O$ requires $H_2O=4.5$ per cent.

$C_{27}H_{46}O$ requires $C=83.9$; $H=11.9$ per cent.

0.3552,* made up to 20 c.c. with chloroform, gave $\alpha_D -1.06'$ in a 2-dcm. tube, whence $[\alpha]_D -30.9^{\circ}$.

The above-described substance was thus identified as a phytosterol. It yielded an acetyl derivative which separated from ethyl acetate in flat needles, melting at $121-122^{\circ}$.

Examination of the Volatile Fatty Acids.

The alkaline, aqueous liquid, from which the unsaponifiable material had been removed by means of ether, as above described, was acidified with sulphuric acid and distilled in a current of steam for ten hours. The combined distillates were then extracted twice with ether, after which the aqueous liquid was made alkaline with barium hydroxide, and evaporated to a low bulk. The excess of alkali was then removed by means of carbon dioxide, the filtered liquid further concentrated, and the acids present investigated by means of the silver salts. Having ascertained that considerable formic acid was present, this was first eliminated by heating the solution with silver nitrate until no further reduction occurred, when, after removing the precipitated silver, four fractions of colourless silver salt were obtained. These fractions, as well as

* Dried at 110° .

the similar ones subsequently referred to, were prepared by adding silver nitrate to a boiling solution of the salts of the volatile acids, when, on cooling the liquid, the silver salts of the organic acid separated in a well-crystallised condition. They were then collected, washed, dried in a vacuum over sulphuric acid, and analysed:

<i>Fraction</i>	I.	0.5286	gave	0.2800	Ag.	Ag=53.0.
„	II.	0.3137	„	0.1700	Ag.	Ag=54.2.
„	III.	0.4012	„	0.2281	Ag.	Ag=56.9.
„	IV.	0.5091	„	0.2979	Ag.	Ag=58.5.
		$C_5H_9O_2Ag$ requires Ag=51.7 per cent.				
		$C_4H_7O_2Ag$	„	Ag=55.4	„	
		$C_2H_3O_2Ag$	„	Ag=64.6	„	

The above results appear to indicate that the volatile acids remaining dissolved in the distillate after extraction with ether consisted of formic, acetic, butyric, and valeric acids.

The ethereal extracts of the distillate were dried and the ether removed, when a quantity (55 grams) of liquid volatile acids was obtained. These acids were carefully fractionated five times under the ordinary pressure, employing a long-necked flask fitted with a rod and disk column, when the following fractions were obtained, all of which were optically inactive: (1) below 160°; (2) 160—170°; (3) 170—180°; (4) 180—190°; (5) 190—200°; (6) 200—210°; (7) 210—220°; (8) 220°+.

Fraction (1) amounted to 1.5 grams, and, since it contained some ether residues, was discarded.

Fraction (2) amounted to 6 grams. A portion of it was nearly neutralised with aqueous potassium hydroxide, and the silver salt prepared from it in four successive fractions. The first of these fractions became reduced owing to the presence of formic acid, but the remainder were analysed, with the following results:

<i>Fraction</i>	II.	0.1564	gave	0.0812	Ag.	Ag=51.9.
„	III.	0.3665	„	0.1895	Ag.	Ag=51.7.
„	IV.	0.3908	„	0.2126	Ag.	Ag=54.4.

A remaining portion of the fraction IV of silver salt was fractionally crystallised, and the more soluble fraction analysed:

	0.4495	gave	0.2474	Ag.	Ag=55.0.
	$C_5H_9O_2Ag$ requires Ag=51.7 per cent.				
	$C_4H_7O_2Ag$	„	Ag=55.4	„	

It thus appears that fraction (2) of the acids consisted essentially of valeric and butyric acids, and since it yielded a calcium salt which was more readily soluble in hot than in cold water, it is evident that the butyric acid present was the *iso*-form.

Fraction (3) amounted to 16 grams. A portion of it was

fractionally converted into the silver salt in the manner previously described, and the resulting 8 fractions analysed:

Fraction	I.	0.5424 *	gave	0.2826 Ag.	Ag=52.1.
„	II.	0.6544	„	0.3370 Ag.	Ag=51.5.
„	III.	0.5709	„	0.2940 Ag.	Ag=51.5.
„	IV.	0.4716	„	0.2429 Ag.	Ag=51.5.
„	V.	0.7109	„	0.3673 Ag.	Ag=51.7.
„	VI.	0.2867	„	0.1488 Ag.	Ag=51.9.
„	VII.	0.7032	„	0.3783 Ag.	Ag=53.8.
„	VIII.	0.7065	„	0.3798 Ag.	Ag=53.8.

These results indicate that fraction (3) of the acids consisted chiefly of valeric acid, together with a little butyric acid. A direct analysis of the fraction gave the following result:

0.1229 gave 0.2588 CO₂ and 0.1068 H₂O. C=57.4; H=9.7.

C₅H₁₀O₂ requires C=58.8; H=9.8 per cent.

C₄H₈O₂ „ C=54.5; H=9.1 „

Fractions (4) and (5) amounted to 4 and 2 grams respectively, and, as they obviously consisted of mixtures of valeric acid and the constituent of fraction (6), they were not further investigated.

Isolation of a Hexenoic Acid, C₆H₁₀O₂.

Fraction (6) of the volatile acids amounted to 20 grams, thus representing more than one-third of the total mixture. It appeared to consist for the most part of an unsaturated substance, since, when dissolved in aqueous alkali, it instantly decolorised a solution of potassium permanganate:

0.1431 gave 0.3279 CO₂ and 0.1168 H₂O. C=62.5; H=9.1.

C₆H₁₀O₂ requires C=63.2; H=8.8 per cent.

C₅H₁₀O₂ „ C=58.8; H=9.8 „

Fraction (6) therefore appeared to consist of a hexenoic acid, contaminated with a very little valeric acid. It was refractionated twice under the ordinary pressure, the following fractions being collected: below 204°; 204—208°; 208°+.

The fraction boiling at 204—208° had D₁₅¹⁵ 0.9833, and was found to consist of a pure hexenoic acid:

0.1150 gave 0.2666 CO₂ and 0.0940 H₂O. C=63.2; H=9.1.

C₆H₁₀O₂ requires C=63.2; H=8.8 per cent.

The silver salt was somewhat sparingly soluble in boiling water, from which it separated, on cooling, in small, colourless leaflets:

0.5854 gave 0.2846 Ag. Ag=48.6.

C₆H₉O₂Ag requires Ag=48.8 per cent.

* This fraction became slightly reduced.

Fraction (7) consisted also of the hexenoic acid, and amounted to 1.5 grams, whilst fraction (8) was so small as to be negligible.

Constitution of the Hexenoic Acid.

In order to ascertain which of the isomeric hexenoic acids the one occurring in hops represented, it was necessary to determine its constitution. A further quantity of the fraction of volatile acids boiling at 200—210° was therefore obtained by working up more of the original petroleum extract of the resin.

A quantity (28 grams) of this approximately pure hexenoic acid was dissolved in an excess of aqueous potassium hydroxide, and gradually treated in the cold with aqueous potassium permanganate until the colour of the latter was only slowly discharged, an amount of oxygen corresponding with a little less than two atomic proportions being thus consumed. The precipitated manganese dioxide was then removed by means of sulphur dioxide, and the clear liquid acidified and distilled in a current of steam for twelve hours. The distillate was rendered alkaline with potassium hydroxide, concentrated to a small bulk, acidified, and then extracted once with ether. This removed about 3 grams of a liquid which was found to consist chiefly of valeric acid, and had doubtless been originally contained in the fraction of acid oxidised. The aqueous liquid from which the valeric acid had been extracted was then distilled with steam, and the acids contained in the distillate converted into the barium salt, from which the silver salt was prepared in three fractions. The first of these fractions was small, and was found to consist of a mixture of silver butyrate and valerate, the former predominating. The second and third fractions, however, which represented by far the greater part of the volatile acid, consisted of silver butyrate (Found, $\text{Ag}=55.3$. Calc., $\text{Ag}=55.4$ per cent.). A quantity of this silver salt was converted into the corresponding calcium salt, which crystallised in tufts of needles, and was much more soluble in hot than in cold water, thus proving it to be calcium *isobutyrate*. It is evident, therefore, that *isobutyric acid* is a product of the oxidation of the hexenoic acid, since not more than a trace of it could have been present in the original fraction of acid boiling at 200—210°.

The original acid liquid remaining after the removal of the above-mentioned volatile acids by distillation with steam, and containing the non-volatile products of the oxidation, was concentrated to a small bulk, and then extracted thirty times with ether. This treatment removed a quantity (about 4 grams) of a solid product which, on fractional crystallisation from a mixture of ethyl acetate and benzene, was found to consist of oxalic acid, together with

another compound, the former predominating. The mixture was therefore converted into the calcium salt, and the calcium oxalate removed and analysed (Found, $\text{CaO} = 43.6$. Calc., $\text{CaO} = 43.8$ per cent.). The filtrate from the calcium oxalate was acidified, and extracted many times with ether, when, on removal of the solvent, a small amount of a crystalline acid was obtained. The latter, on recrystallisation from benzene containing a little ethyl acetate, separated in colourless leaflets, melting at 109° :

0.0787 * gave 0.1404 CO_2 and 0.0586 H_2O . $\text{C} = 48.6$; $\text{H} = 8.3$.

$\text{C}_6\text{H}_{12}\text{O}_4$ requires $\text{C} = 48.6$; $\text{H} = 8.1$ per cent.

This acid was thus identified as $\alpha\beta$ -dihydroxyisohexenoic acid, $\text{CH}_3 \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$, which has been described by Braun (*Monatsh.*, 1896, **17**, 216) as melting at 108° . On oxidation with chromic acid, it yielded isobutyric acid.

From the results of the above-described oxidation, it is evident that the hexenoic acid contained in hops is β -isopropylacrylic acid, $\text{CH}_3 \cdot \text{CH}(\text{CH}_3) \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H}$, a substance which has not previously been known to occur in nature. It has an odour resembling that of valeric acid, but somewhat more rank.

Isolation of a Phytosterolin, $\text{C}_{33}\text{H}_{56}\text{O}_6$.

The original alkaline solution obtained by the hydrolysis of the petroleum extract of the resin, and from which the volatile acids had been removed, as above described, was shaken with a large volume of ether, when a relatively small quantity of a sparingly soluble solid remained undissolved. This was collected, washed with ether, and then extracted in a Soxhlet apparatus, first with ethyl acetate until the chlorophyll was removed, and subsequently for a long time with alcohol. The solid which gradually separated from the latter solvent during the process of extraction was collected, and heated with acetic anhydride containing a little pyridine, when, on removing the greater part of the solvent, a product was obtained which crystallised from alcohol in colourless leaflets. This was hydrolysed with alcoholic potassium hydroxide, when it yielded a substance which separated from dilute pyridine in colourless, microscopic crystals, melting at $285\text{--}290^\circ$:

0.1147 gave 0.3039 CO_2 and 0.1084 H_2O . $\text{C} = 72.3$; $\text{H} = 10.5$.

$\text{C}_{33}\text{H}_{56}\text{O}_6$ requires $\text{C} = 72.3$; $\text{H} = 10.2$ per cent.

0.1918, made up to 20 c.c. with pyridine, gave $\alpha_D - 0^\circ 37'$ in a 2-dcm. tube, whence $[\alpha]_D - 32.1^\circ$.

This substance was thus identified as a phytosterolin, or phytosterol glucoside (compare Power and Salway, this vol., p. 399).

* Dried at 90° .

The acetyl derivative melted at 167—168°, and was analysed:

0.1049 gave 0.2648 CO₂ and 0.0862 H₂O. C=68.9; H=9.1.

C₃₃H₅₂O₆(CO·CH₃)₄ requires C=68.7; H=8.9 per cent.

The benzoyl derivative, prepared by benzylation in pyridine solution, crystallised from a mixture of chloroform and alcohol in slender, colourless needles, melting at 198°:

0.0959 gave 0.2673 CO₂ and 0.0667 H₂O. C=76.0; H=7.7.

C₃₃H₅₂O₆(CO·C₆H₅)₄ requires C=75.9; H=7.5 per cent.

*Half a gram of the phytosterolin was hydrolysed in amyl alcohol solution by heating with aqueous hydrogen chloride, together with sufficient ethyl alcohol to render the mixture homogeneous, when it yielded dextrose together with a phytosterol. The latter formed glistening leaflets, melting at 136°:

0.1041 gave 0.3204 CO₂ and 0.1127 H₂O. C=83.9; H=12.0.

C₂₇H₄₆O requires C=83.9; H=11.9 per cent.

Examination of the Non-volatile Fatty Acids.

The ethereal solution from which the crude phytosterolin had been removed by filtration was evaporated, when a very dark green, viscid product was obtained, representing the greater portion of the original petroleum extract of the resin. It was dissolved in methyl alcohol, esterified by means of sulphuric acid, and the resulting product extracted with ether. The ethereal solution was then shaken with a large volume of aqueous 25 per cent. potassium hydroxide, after which the mixture separated into three layers. The lowest layer was an orange-coloured, aqueous liquid, and, when separated and acidified, yielded about 10 grams of a viscid, orange-coloured product, which possessed a somewhat bitter taste, but afforded nothing definite. The middle layer consisted of an almost black, viscid tar, and was found to consist of the potassium compound of a phenolic resin. The latter, when isolated, formed a dark greenish-brown resin, which amounted to about one-third of the total product; it was tasteless, and nothing definite could be obtained from it. The ethereal layer, on evaporation, yielded a dark green oil, consisting of the methyl esters of the fatty acids contaminated with chlorophyll. It was deprived of the latter by distillation under diminished pressure, after which the distillate was hydrolysed, the resulting fatty acids extracted with ether, and separated into their saturated and unsaturated components by means of their lead salts, in the usual manner.

* This experiment was conducted by Dr. Salway.

The Saturated Fatty Acids.

The acids obtained from the insoluble lead salts were esterified by means of methyl alcohol and sulphuric acid, and the resulting esters carefully fractionated five times under a pressure of 20 mm., with the employment of a long-necked flask, when the following fractions were collected: (1) below 205°; (2) 205—210°; (3) 210—215°; (4) 215—220°; (5) 220—225°; (6) 225—235°; (7) above 235°/20 mm.

Fractions (1) and (2) solidified on cooling, and represented the greater part of the material. They both consisted of practically pure methyl palmitate, and, on hydrolysis, yielded palmitic acid, which, after crystallisation, melted at 62·5° (Found, C=74·8; H=12·5. Calc., C=75·0; H=12·5 per cent.).

Fraction (3) was hydrolysed, but the resulting acid, even after very many crystallisations, did not appear homogeneous, and melted at 61—64·5°. It appeared to consist of a mixture of palmitic and stearic acids in about equal proportions (Found, C=75·6; H=12·6. Calc. for $C_{16}H_{32}O_2$, C=75·0; H=12·5; for $C_{18}H_{36}O_2$, C=76·1; H=12·6 per cent.).

Fraction (4) was small in amount, and, on hydrolysis, yielded an acid which, after crystallisation, melted at 66—67°, and was nearly pure stearic acid (Found, C=76·2; H=12·7. Calc., C=76·1; H=12·6 per cent.).

Fraction (5) was also small in amount. On hydrolysis, it yielded an acid which, when repeatedly crystallised from various solvents, appeared perfectly homogeneous. It formed glistening plates, melting constantly at 62·5—63°:

0·1098 gave 0·3088 CO_2 and 0·1272 H_2O . C=76·7; H=12·9.

$C_{20}H_{40}O_2$ requires C=76·9; H=12·8 per cent.

This acid is thus seen to agree in composition with arachidic acid, the melting point of which, however, has been recorded as 77°. It therefore appears probable that it is an isomeride of arachidic acid, and in that case would be a new compound. The results given above were confirmed by working up a further and larger amount of the original petroleum extract of the resin, but the total amount of the respective acid obtained was not sufficient conclusively to establish its homogeneity, although it had all the characters of a pure substance.

Isolation of Cluytinic Acid, $C_{21}H_{42}O_2$.

Fraction (6) was larger in amount than either of the two fractions immediately preceding it. It was hydrolysed, and the resulting

acid crystallised several times, when it formed lustrous leaflets, melting constantly at 69° :

0.0996 gave 0.2826 CO_2 and 0.1176 H_2O . $\text{C}=77.3$; $\text{H}=12.9$.

$\text{C}_{21}\text{H}_{42}\text{O}_2$ requires $\text{C}=77.3$; $\text{H}=12.9$ per cent.

This acid thus appeared to be identical with cluytinic acid, a compound which was only recently obtained by Tutin and Clewer from the South African plant, *Cluytia similis* (T., 1912, **101**, 2226). In order to exclude any possibility of doubt regarding its homogeneity, it was compared with all possible mixtures of higher and lower fatty acids having the same percentage composition, but the latter products were all of lower and indefinite melting point. Further evidence of the identity of the substance with cluytinic acid was afforded by working up an additional quantity of the original petroleum extract of the resin, when an acid was obtained which possessed the same composition and properties as that above described. Moreover, a quantity of the acid was converted into its methyl ester, and the latter crystallised several times from alcohol, when it was found to be homogeneous.

Methyl Cluytinate, $\text{C}_{20}\text{H}_{41}\cdot\text{CO}_2\cdot\text{CH}_3$.—This compound forms small, colourless, lustrous leaflets, melting sharply at 47° :

0.0930 gave 0.2640 CO_2 and 0.1087 H_2O . $\text{C}=77.4$; $\text{H}=13.0$.

$\text{C}_{22}\text{H}_{44}\text{O}_2$ requires $\text{C}=77.6$; $\text{H}=12.9$ per cent.

Isolation of Cerotic Acid.

Fraction (7) was a solid of appreciably higher melting point than any of the preceding fractions. It was crystallised successively from ethyl acetate and alcohol, when it separated in small, colourless leaflets, melting sharply at 58° , and evidently consisted of methyl cerotate. On hydrolysis, it yielded cerotic acid, which crystallised in small, colourless plates, melting at 79° (Found, $\text{C}=78.7$; $\text{H}=13.2$. Calc., $\text{C}=79.0$; $\text{H}=13.2$ per cent.).

The Unsaturated Fatty Acids.

The unsaturated fatty acids were regenerated from the soluble lead salts, and extracted with ether. They represented the largest individual product obtained from the hop extract, being about three times as great in amount as the saturated acids.

A portion of the material was converted into the methyl ester, and the latter fractionally distilled six times under 20 mm. pressure, with the employment of a long-necked flask, when the following fractions were collected, and in the amounts indicated: I, below 215° (9.7 grams); II, 215 — 218° (29.5 grams); III, 218 — 222° (94.1 grams); IV, 222 — $227^{\circ}/20$ mm. (4.5 grams). These fractions

were analysed, and their iodine values determined, with the following results:

Fraction	I.	C=76.1; H=11.6.	Iodine value=150.6.
„	II.	C=77.3; H=11.5.	Iodine „ =172.2.
„	III.	C=77.2; H=11.5.	Iodine „ =177.3.
„	IV.	C=77.1; H=11.4.	Iodine „ =164.4.

Methyl linolate, $C_{19}H_{34}O_2$, requires C=77.5; H=11.5 per cent.
I.V.=172.7.

It thus appears that the unsaturated acids consisted almost entirely of linolic acid. The somewhat low figures obtained for the first fraction of esters was probably due to the presence of a little methyl palmitate.

Ether Extract of the Resin.

This extract, when free from solvent, formed a dark green, friable mass. A portion of the ethereal solution of the extract, representing 170 grams of dry material, was largely diluted with ether, when a quantity (about 18 grams) of a dark brown solid was precipitated. The latter was found to consist only of brown resin, together with a little phytosterolin. The filtrate was shaken with aqueous ammonium carbonate, and the alkaline liquid separated and acidified. A quantity of green, tarry material was thus obtained, which had a very bitter, nauseous taste, and an odour resembling that of valeric acid. As nothing definite could be directly separated from it, it was heated with alcoholic potassium hydroxide for some time, the alcohol then removed, water added, and the mixture acidified and distilled with steam. Nothing definite could be isolated from the contents of the distillation flask, but the distillate yielded about 2 grams of volatile acid. The latter distilled from 110° to about 245° under the ordinary pressure, and, after removing a little formic acid, the silver salt was prepared from it in three fractions. A small proportion of an unsaturated acid was present, which was doubtless the previously described hexenoic acid:

Fraction	I.	0.1335 gave 0.0543 Ag.	Ag=40.7.
„	II.	0.4597 „ 0.2321 Ag.	Ag=50.5.
„	III.	0.2453 „ 0.1245 Ag.	Ag=50.8.
		$C_9H_{17}O_2Ag$ requires	Ag=40.7 per cent.
		$C_8H_{11}O_2Ag$ „	Ag=48.4 „
		$C_6H_9O_2Ag$ „	Ag=48.8 „
		$C_5H_9O_2Ag$ „	Ag=51.7 „

The mixture of volatile acids obtained from the ether extract of

the resin therefore appears to have contained nonoic, hexenoic, and valeric acids, but other acids may also have been present.

The ethereal liquid which had been extracted with ammonium carbonate, as above described, was washed with water, when some chlorophyll was removed, and subsequently shaken with a considerable volume of fairly concentrated aqueous sodium carbonate. The mixture then separated into three layers, and the lowest layer, which was a deep yellow, aqueous liquid, was separated and acidified as quickly as possible. The mixture remaining in the separator, which consisted of a green, ethereal liquid, together with a large quantity of a black, tarry sodium compound of a resin beneath it, was then extracted many times with aqueous sodium carbonate, the alkaline liquids being in each case acidified as soon as possible.

Isolation of a New Phenolic Substance, Humulol, $C_{17}H_{18}O_4$.

The combined, acidified sodium carbonate extracts above mentioned were extracted with ether, and the ethereal solution fractionally extracted with alkalis in order to effect a more exact separation of its constituents. On shaking with ammonium carbonate, a quantity of a brownish-yellow resin was removed, and, since the original material had been deprived of substances soluble in this alkali, it must have been formed by the action of the sodium carbonate on some constituent originally present. It possessed a somewhat bitter taste, but nothing could be isolated from it. The ethereal solution was then shaken with a small quantity of very dilute, aqueous sodium carbonate, and subsequently washed with water. This treatment removed some green, resinous material and a quantity of chlorophyll. The ethereal liquid was subsequently extracted with many successive portions of concentrated aqueous sodium carbonate, the resulting alkaline extracts being quickly separated and acidified, when they were separately examined. The first three extractions yielded a product which, when isolated by means of ether and the resulting ethereal solution concentrated, deposited a quantity of a crystalline substance. The total amount of this substance obtained in the present instance and from the remaining quantity of ether extract of the resin was altogether about 5.6 grams, being thus equivalent to 0.0224 per cent. of the weight of hops employed. The crystalline substance was collected on a filter, and washed with ether, after which it was recrystallised by concentrating its solution in ether containing a little alcohol. As thus obtained, it formed small, almost colourless needles, which, when dissolved in alcohol, possessed a bitter taste. Various separately isolated portions of this substance

exhibited different behaviour on heating. Thus, most of them melted at about $150\text{--}154^\circ$, with the evolution of gas, whilst others only sintered at this temperature, fusion occurring at about 194° . All the different quantities of bitter substance obtained gradually became yellow, however, when heated at 90° , after which they melted at about 140° , and when heated for half an hour at 135° they appeared to decompose, being converted into an orange-coloured resin and suffering a diminution in weight. It was found, however, that this behaviour was due to the presence of varying amounts of ether of crystallisation, since when the substance was recrystallised from 50 per cent. acetic acid, it formed small, pale fawn-coloured needles, which, when heated fairly quickly, melted at 196° , and did not change at 135° . On again recrystallising from ether, the product of low melting point was regenerated. A very careful examination of the substance proved it to be quite homogeneous, and, after crystallisation from dilute acetic acid, it was analysed:

0.1105 * gave 0.2880 CO_2 and $0.0634\text{ H}_2\text{O}$. $\text{C} = 71.1$; $\text{H} = 6.4$.

0.1144 * „ 0.2972 CO_2 „ $0.0653\text{ H}_2\text{O}$. $\text{C} = 70.9$; $\text{H} = 6.3$.

0.3550, in 29.02 of acetic acid, gave $\Delta t - 0.175^\circ$, whence $\text{M.W.} = 273$.

$\text{C}_{17}\text{H}_{18}\text{O}_4$ requires $\text{C} = 71.3$; $\text{H} = 6.3$ per cent. $\text{M.W.} = 286$.

It is evident from these results that the above-described substance possesses the formula $\text{C}_{17}\text{H}_{18}\text{O}_4$. As it does not agree with any substance of this formula hitherto described it is undoubtedly a new compound, and, with reference to its phenolic properties and its source, it is proposed to designate it *humulol*.

Humulol dissolves in aqueous sodium carbonate, but not in ammonium carbonate or hydroxide. Its solution in alkali is pale yellow, but becomes deep yellow when kept for some time, or when warmed. It dissolves in concentrated sulphuric acid, yielding a pale yellow liquid, and, in alcoholic solution, gives no coloration with ferric chloride. It is insoluble in water, light petroleum, or benzene, very sparingly soluble in ether or chloroform, moderately so in glacial acetic acid, and very readily so in alcohol or pyridine. On acetylation, it yielded a colourless product, which, however, was a viscid, uncrystallisable liquid.

Hydrolysis of Humulol: Formation of p-Hydroxybenzaldehyde.

About 3 grams of humulol were dissolved in 20 per cent. aqueous potassium hydroxide, and the solution boiled for half an hour. The liquid first became deep yellow, but subsequently much lighter in colour. It was acidified, and extracted several times with ether,

* Dried at 135° .

the ethereal liquid being then extracted successively with aqueous ammonium carbonate, sodium carbonate, and potassium hydroxide.

The alkaline liquid obtained by extraction with ammonium carbonate yielded, on acidification and extraction with ether, a small amount of a crystalline product, which evidently was an acid. This was recrystallised from benzene, when it was obtained in small, nearly colourless prisms, melting at 210° :

0.0697 gave 0.1676 CO_2 and 0.0324 H_2O . $\text{C}=65.6$; $\text{H}=5.2$.

$\text{C}_{15}\text{H}_{14}\text{O}_5$ requires $\text{C}=65.7$; $\text{H}=5.1$ per cent.

This acid would thus appear to possess the formula $\text{C}_{15}\text{H}_{14}\text{O}_5$, and in that case would be a new compound. The amount obtained, however, was not sufficient for its further examination.

The sodium carbonate extract yielded, on acidification and extraction with ether, a larger amount of material. It was crystallised first from benzene and subsequently from water, when colourless needles were obtained, melting at 118° :

0.0860 gave 0.2168 CO_2 and 0.0393 H_2O . $\text{C}=68.8$; $\text{H}=5.1$.

$\text{C}_7\text{H}_6\text{O}_2$ requires $\text{C}=68.9$; $\text{H}=4.9$ per cent.

This substance yielded a dark violet colour with ferric chloride, and was identified as *p*-hydroxybenzaldehyde. When mixed with an authentic specimen of the latter compound, the melting point remained unchanged.

The potassium hydroxide extract of the ethereal solution of the hydrolytic products yielded, on extraction with ether, a pale brown, viscid product, which could not be crystallised, and gave no coloration with ferric chloride. It yielded an oily acetyl derivative, and when methylated by means of methyl sulphate and potassium hydroxide, a similar oily product was obtained. On distilling the latter under diminished pressure, however, it was found not to be homogeneous, but the amount available did not permit of its further investigation.

Isolation of a New Yellow Phenolic Substance, Xanthohumol,
 $\text{C}_{13}\text{H}_{14}\text{O}_3$.

As previously mentioned, the above-described substance, humulol, was isolated from the liquids obtained by the first three extractions with concentrated aqueous sodium carbonate. Most of the subsequently obtained sodium carbonate extracts, however, also yielded small amounts of humulol, which was readily separated on account of its sparing solubility in pure ether. On examining the filtrates from these small residual amounts of humulol, it was found that they contained a second substance, which was only very slowly removed from its solution in ether by fairly concentrated aqueous sodium carbonate, but much more readily by potassium hydroxide.

The total amount of material readily soluble in pure ether, obtained from all but the first three extractions with aqueous sodium carbonate, was brought together, and the ether removed. A small amount of alcohol was then added to the green, viscid residue, and the mixture kept for some days, when crystallisation gradually ensued. The green, viscid mixture containing the crystalline solid was then drained on a porous tile in an atmosphere saturated with alcohol, when a deep orange-coloured, crystalline substance was obtained. The latter was crystallised from a small volume of alcohol, when it formed glistening, orange-coloured, acicular crystals, melting at 169.5° :

0.1071 * gave 0.2790 CO_2 and 0.0613 H_2O . $\text{C}=71.0$; $\text{H}=6.4$.

An additional amount of this compound was obtained in a similar manner from a further quantity of the original ether extract of the resin, and was crystallised three times from alcohol. It then melted constantly at 172° :

0.0855 gave 0.2239 CO_2 and 0.0495 H_2O . $\text{C}=71.4$; $\text{H}=6.4$.

$\text{C}_{13}\text{H}_{14}\text{O}_3$ requires $\text{C}=71.5$; $\text{H}=6.4$ per cent. $\text{M.W.}=218$.

A determination of the molecular weight of the substance by Barger's microscopic method was kindly made for us by Mr. A. J. Ewins, with the following result:

0.0554, in 1.172 of pyridine, using benzil as the standard, was between 0.225 and 0.250 mol. Mean $\text{M.W.}=184$.

It would appear from the above results that the orange-coloured substance possesses the formula $\text{C}_{13}\text{H}_{14}\text{O}_3$. Since it differs in its properties from any known substance of this composition, it is evidently a new compound, and, with consideration of its characters and its source, it is proposed to designate it *xanthohumol*.

Xanthohumol, although possessing practically the same percentage composition as the previously described compound, humulol, is not an isomeride of the latter, as is shown by the determination of their respective molecular weights. The two compounds are, moreover, quite different in their properties. Thus, xanthohumol is devoid of bitter taste, and is not decomposed by heating with alkalis, but dissolves in the latter with an intense yellow colour. In alcoholic solution it gives no coloration with ferric chloride. When dissolved in sulphuric acid it yields at first a very deep orange-coloured liquid, which, however, soon becomes nearly colourless. It is very readily soluble in ether, ethyl acetate, or pyridine, moderately so in alcohol, and rather sparingly so in benzene or glacial acetic acid. On acetylation or methylation, it yielded only

* Dried at 135° .

viscid, uncrystallisable oils. The total amount of xanthohumol obtained was about 2 grams, being thus equivalent to about 0.008 per cent. of the weight of hops employed.

The alcoholic mother liquors from the first recrystallisation of the xanthohumol, when slowly evaporated, were found to contain a small amount of yet another compound. The latter formed very small, pale yellow needles, but the amount present was not sufficient to permit of its further characterisation.

The original ethereal solution of the ether extract of the resin, which had been extracted many times with aqueous sodium carbonate, as previously described, was separated from the large amount of black, tarry material which had been produced during the extractions with alkali. This dark-coloured material, which possessed a somewhat bitter taste, was entirely resinous in character, and nothing could be isolated from it. The ethereal solution, however, on extraction with aqueous potassium hydroxide, yielded a further small amount of the previously described humulol, together with amorphous products. The final ethereal solution of the neutral constituents of the resin was evaporated, and the residue, from which nothing definite could be directly separated, was heated with alcoholic potassium hydroxide. This treatment, however, led only to the isolation of a further small amount of the previously mentioned phytosterolin, together with chlorophyll and amorphous products.

Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

The chloroform, ethyl acetate, and alcohol extracts of the resin were all amorphous solids, which, when dissolved in alcohol, possessed a somewhat bitter taste. The chloroform extract had a dull green colour, but the last-mentioned two extracts were dark brown. All of these extracts were examined, but nothing definite could be isolated from them, and, on heating with dilute sulphuric acid in aqueous alcohol, they were found to contain nothing glucosidic.

Summary and Conclusions.

The material used in this investigation consisted of a good quality of fresh Kentish hops of the crop of 1911.

The air-dried material contained 10.48 per cent. of moisture, 2.4 per cent. of tannin, and, on incineration, yielded 7.919 per cent. of ash.

For the purpose of a complete examination, 25 kilograms of hops were employed. This material was ground, completely extracted

with hot alcohol, and the resulting extract distilled in a current of steam in order to remove the essential oil.

From the portion of the extract which was soluble in water there were isolated small amounts of choline, $C_5H_{15}O_2N$, and of *l*-asparagine, $C_4H_8O_3N_2$, both of which had previously been observed to be present, although no evidence of the identity of the last-mentioned substance appears to have hitherto been recorded. The aqueous liquid also contained, besides tannin, a quantity of potassium nitrate and a sugar which yielded *d*-phenylglucosazone (m. p. 208°), together with dark-coloured, amorphous material which possessed an intensely bitter taste. A volatile base, having a coniine-like odour, was also obtained, but the amount was so extremely small that it could not be further characterised.

The portion of the alcoholic extract which was insoluble in water consisted of a dark green, oily resin, the amount of which was equivalent to about 14.1 per cent. of the weight of hops employed. From this resin, which still contained some occluded essential oil, the following compounds were isolated: (i) ceryl alcohol, $C_{27}H_{56}O$; (ii) hentriacontane, $C_{31}H_{64}$; (iii) a phytosterol, $C_{27}H_{46}O$; (iv) a phytosterolin (phytosterol glucoside), $C_{33}H_{56}O_6$; (v) a mixture of volatile fatty acids, consisting of formic, acetic, butyric, and valeric acids, together with a hexenoic acid, $C_6H_{10}O_2$ (b. p. $204-208^\circ$), which was identified as β -isopropylacrylic acid, and apparently a little nonoic acid, $C_9H_{18}O_2$, was also present; (vi) saturated and unsaturated non-volatile acids, comprising: palmitic, stearic, and cerotic acids, and an acid, $C_{20}H_{40}O_2$ (m. p. $62.5-63^\circ$), which is apparently an isomeride of arachidic acid; furthermore, cluytinic acid, $C_{21}H_{42}O_2$ (m. p. 69°), the *methyl* ester of which melts at 47° , and linolic acid; (vii) a new, crystalline, phenolic substance, *humulol*, $C_{17}H_{18}O_4$ (m. p. 196°), possessing a pale fawn colour and a bitter taste, which, on hydrolysis with potassium hydroxide, yielded, among other products, an acid, $C_{15}H_{14}O_5$ (m. p. 210°), and *p*-hydroxybenzaldehyde; (viii) a new, crystalline, phenolic substance, *xanthohumol*, $C_{13}H_{14}O_3$ (m. p. 172°), which is tasteless and possesses an orange-yellow colour. The statements made many years ago that hops contain a yellow colouring matter resembling quercitrin, and also a wax consisting of myricyl palmitate, cannot be confirmed.

A consideration of the results of the present investigation leads to the following conclusions. In the first place, the bitterness of hops is not due to any single substance, such as the so-called "hop-bitter acid" or "lupulic acid," but is to be attributed to a number of products, most of which are amorphous. Some of these products are soluble in water, whilst others represent constituents of the

resin. One well-defined, crystalline substance, which possesses a bitter taste, has, however, now been isolated from the resin, and, as above noted, has been designated *humulol*. Furthermore, the differentiation of the resinous material as α -, β -, and γ -resins is misleading, inasmuch as this material is much more complex in character than would be indicated by the methods employed for the separation of the respective products.

It may finally be noted that, although various products have hitherto been obtained from hops which were supposed to represent the bitter principles, the characters ascribed to them renders it evident that they were of a very indefinite nature. On the other hand, all previous investigators appear completely to have overlooked the important fact that the resinous material contains a large proportion of the ordinary fatty acids and their esters. Such of the numerous methods proposed for the valuation of hops as are based on the titration of extracts obtained by means of light petroleum and similar solvents are therefore of very doubtful utility.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CXXXVI.—*The Preparation and Analysis of Methane.*

By COLIN CAMPBELL and ALBERT PARKER.

ALTHOUGH many investigations have been carried out in which methane has played a prominent part, a convenient method of preparation of the pure gas has not previously been devised. Moreover, the analysis of methane has been troublesome or inaccurate.

Capstick (*Phil. Trans.*, 1894, A, 185, 1) attempted to prepare pure methane by two methods. The first method was that devised by Gladstone and Tribe, and consisted of treating a mixture of methyl iodide and alcohol with the zinc-copper couple. The gas obtained was purified from methyl iodide by passing through fuming sulphuric acid, and any sulphur dioxide thus produced was removed by means of potassium hydroxide. The methane purified in this way was found to contain hydrogen, and to free it from this impurity the gas was passed over palladium black. The absorption of hydrogen by palladium was, however, found to be unsatisfactory.

An analysis of the methane prepared in the above way was

made, by explosion with oxygen, and the following results were obtained:

	Vols.	Calculated impurity.
		Per cent.
Gas taken	100·61	
Contraction	98·97	1·64
2		
Contraction after potash	99·43	1·18

From this analysis it will be seen that the amounts of impurity (assumed to be air) obtained from explosion and absorption by potassium hydroxide differed by 0·46 per cent. Capstick's second method consisted in dropping a mixture of zinc methyl and ether on to water. In this case the reaction was found to be very violent, and the product contained 1·4 per cent. of air. Capstick also found that methane could not be purified from air by liquefaction, since air is fairly soluble in liquid methane.

Moissan and Chavanne (*Compt. rend.*, 1905, **140**, 407) prepared pure aluminium carbide, and decomposed this by water. The methane obtained was liquefied and then fractionally distilled. Analysis by explosion gave the following results:

	Vols.	Impurity (assumed to be air).
		Per cent.
Gas taken	2·85	
Contraction	2·825	0·9
2		
Contraction after potassium hydroxide	2·80	1·7

The object of the following experiments was to devise a convenient method of preparation of pure methane in comparatively large quantities, about 100 litres being required. At the same time, it was found necessary to devise an accurate method of analysis of methane, especially for traces of hydrogen.

Preparation of Methane from Zinc Methyl.

In the first method employed, zinc methyl was allowed to drop slowly into a large volume of cold water. The air contained in the apparatus was previously displaced by carbon dioxide, which was afterwards removed from the methane by means of sodium hydroxide solution. Analysis showed the gas prepared in this way to contain ethane and air as impurities, and, as Capstick had previously observed, it was almost impossible to purify methane from these substances.

Preparation of Methane from Aluminium Carbide.

It was then decided to examine the gas produced on decomposition of aluminium carbide by water. Since ordinary commercial aluminium carbide gives a very impure product when

decomposed by water, a comparatively pure sample of fused carbide was first obtained. It consisted of exceedingly hard, bright yellow lumps, and contained some free aluminium as impurity. The carbide was first broken up into small pieces about the size of a pea.

In the first few experiments about 100 grams of carbide were placed in a 500 c.c. flask, and cold water allowed to enter from a tap funnel. The reaction at the commencement was inappreciable. The flask was then heated to 80° , when gas began to be evolved, and finally the reaction became fairly violent. The amount of heat generated was so great that the material became hot and dry, and invariably cracked the flask. Finally, the following was found to be the most convenient method of decomposition of aluminium carbide. About 100 grams of carbide were placed in a small flask, and covered with about 350 c.c. of previously boiled water at 90° . The reaction commenced slowly, and developed until a steady evolution of gas ensued. The impure gas was then passed through two wash-bottles containing an ammoniacal solution of cuprous chloride. This was to remove acetylene, which was found to be present in very small quantities. The ammonia which passed over from the cuprous chloride solution was removed by means of dilute sulphuric acid contained in a large wash-bottle. The gas obtained in this way was quite odourless, and was collected over water and analysed. The results of analysis, by exploding with about four times its volume of oxygen, gave a contraction less than twice the volume of the gas taken, and after absorption with potassium hydroxide, the contraction was less than half that obtained by explosion. Since the free aluminium contained in the carbide might have decomposed the water, giving free hydrogen, the gas was analysed for this impurity by mixing with oxygen and passing over palladium black. (The method of analysis is subsequently described in detail).

The following result was obtained :

Gas taken	19.58
Gas + oxygen	28.05
After passing over palladium ...	26.20

Contraction.....	1.85 representing 6.3 per cent. of hydrogen.
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The gas therefore contained 6.3 per cent. of hydrogen.

An attempt was made to remove the hydrogen by liquefying the methane by liquid air. Sufficient methane was then boiled to displace the gas contained in the apparatus, and the remainder was collected and analysed.

Analysis showed the product to contain 3 per cent. of hydrogen. This proves that hydrogen is soluble in liquid methane. A mixture containing 80 per cent. of methane and 20 per cent. of hydrogen

was afterwards made, and liquefied by means of liquid air. As a result, it was found that nearly one-half of the liquefied methane had to be boiled away before the product was free from hydrogen.

It was then decided to attempt to burn out the hydrogen by adding a slight excess of oxygen and passing the mixture over palladium black. A careful analysis of the gas was made for hydrogen, and rather more than the calculated quantity of pure oxygen added. The mixture was then passed at the rate of one litre per hour through two wash-bottles containing concentrated sulphuric acid to dry the gas, through a series of bulbs containing palladium black heated to 100° , and through potassium hydroxide to remove sulphur dioxide. The excess of oxygen was removed by means of alkaline pyrogallol solution. The composition of the alkaline pyrogallol solution was that recommended by Hempel, so that the evolution of carbon monoxide was avoided. A careful analysis of the product was afterwards made, and the following results were obtained.

(A)	Gas taken	25.17	
	Gas + air	29.85	
	After passing over palladium	29.85	
	Contraction.....	0.0	hydrogen was therefore absent.
(B)	Gas taken	18.2	
	After pyrogallol	18.19	
	Contraction	0.01	oxygen was therefore absent.
(C)	Gas taken	5.0	
	Gas + oxygen	27.36	
	After explosion	17.46	
	Contraction	9.90	
	After potassium hydroxide	12.50	C/2 4.95
	Absorption.....	4.96	A 4.96.

The gas therefore contained 0.8 per cent. of nitrogen. A sample of methane has since been prepared by the above method, and analysis showed it to be free from hydrogen; oxygen and even nitrogen could not be detected. The following result was obtained on analysis:

Gas taken	4.99	
Gas + oxygen	23.30	
After explosion	13.33	
Contraction.....	9.97	
After potassium hydroxide	8.33	C/2 4.985
Absorption	5.0	A 5.0

We have prepared by this method over 100 litres of pure methane.

Analysis of Methane.

A Bone and Wheeler gas analysis apparatus was used to analyse the various samples of methane obtained. In the first analyses

carried out, the gas was mixed with about four times its volume of oxygen, and the mixture exploded under diminished pressure. The contractions in volume after explosion and after a subsequent treatment with potassium hydroxide solution were recorded. This method, however, could not be used accurately to estimate the hydrogen contained in the methane. An attempt was first made to burn away the hydrogen by means of a heated platinum spiral contained in the laboratory vessel of the Bone and Wheeler apparatus. The gas to be analysed was mixed with a small quantity of oxygen, and the mixture was passed into the laboratory vessel and exposed to the platinum spiral, which was heated to a just visible red heat. Some of the methane was found to burn on the surface of the platinum, and discordant results were obtained.

It was then decided to attempt the analysis of the methane and hydrogen mixture by first adding oxygen and then passing the mixture several times over palladium black at 90° to 100° .

The apparatus used consists essentially of a Bone and Wheeler gas analysis machine. The palladium is contained in a small bulb, heated in a water-bath to 100° , and connected on the one side to a small laboratory vessel, and on the other to the measuring vessel. Between the palladium bulb and measuring vessel, a second bulb is inserted to catch any mercury which accidentally passes over. This is necessary, since if palladium black comes into contact with any mercury, it loses its power of producing the combination of hydrogen and oxygen. By means of a three-way tap, the measuring vessel can be connected with the main laboratory vessel of the apparatus, or with the palladium bulb.

Previous to carrying out an analysis, it is necessary completely to exhaust the apparatus containing the palladium. This is done by first removing all gas from the rest of the analysis apparatus, and then connecting the exhausted measuring vessel with the palladium bulb. The three-way tap is closed, and the measuring vessel again exhausted. By repeating this three or four times, all the gas contained in the palladium bulb is pumped out, as the measuring vessel has a capacity of about twenty times that of the palladium bulb. The gas to be analysed is then measured and mixed with a small quantity of oxygen. The mixture is passed slowly over the palladium two or three times. The whole of the gas is then pumped into the main laboratory vessel, passed back into the apparatus and measured. From the observed contraction in volume, the amount of hydrogen can be estimated. This method of estimation of hydrogen in methane was found to be very satisfactory and gave constant results.

Addendum.—Since this paper was written, J. Harger (*Colliery*

Guardian, March, 1913) has described a method of preparation of methane from aluminium carbide, the hydrogen being removed by passing the gas over copper oxide at 160°.

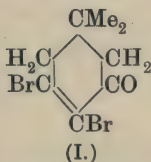
THE UNIVERSITY,
MANCHESTER.

CXXXVII.—*Derivatives of o-Xylene. Part V. 5-Bromo-o-4-xyleneol and 6-Bromo-o-4-xyleneol.*

By ARTHUR WILLIAM CROSSLEY and DOROTHY JESSIE BARTLETT.

REFERENCE has already been made to the fact that a monobromoxyleneol, melting at 103°, has been obtained by the action of phosphorus pentabromide on dimethyldihydroresorcin (P., 1912, **28**, 333), at which time its constitution had not been settled, although it seemed certain that it was a derivative of *o*-4-xyleneol, because on treatment with bromine it gave a tribromoxyleneol, and from this an acetyl derivative, the melting points of which were not lowered on admixture respectively with tribromo-*o*-4-xyleneol and its acetyl derivative.

More recently this same bromoxyleneol has been obtained by the action of heat on dibromodimethylcyclohexenone (I), the con-

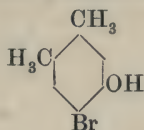


stitution of which substance is settled by its method of preparation (compare this vol., p. 989), and consequently a more definite clue as to the constitution of the bromoxyleneol was indicated.

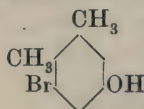
During the conversion of dibromodimethylcyclohexenone: (a) one of the bromine atoms must be eliminated as hydrogen bromide, thus the resulting bromoxyleneol certainly contains the bromine atom in one of two positions, 4 or 5; (b) the ketone group must become hydroxylic, thus fixing the position of the phenolic group; (c) a methyl group must wander, and since the resulting bromoxyleneol is a derivative of *o*-4-xyleneol, the methyl group must have taken up position 6 and not position 2, as in previously recorded cases (compare T., 1902, **81**, 1533; 1904, **85**, 264; 1906, **89**, 875; 1908, **93**, 633). It is therefore obvious that the

bromoxylanol must have one or other of the two formulæ II or III.

In the first place, 5-bromo-*o*-4-xylanol (II) was synthesised by

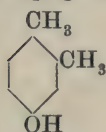


(II.)

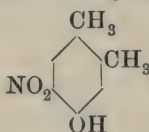


(III.)

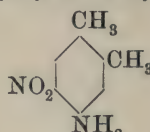
the following series of reactions. Diepolder (*Ber.*, 1909, **42**, 2916) has shown that the direct nitration of *o*-4-xylanol (IV) gives rise to 5-nitro-*o*-4-xylanol (V), because when the latter substance is heated with ammonia the hydroxyl group is replaced by an amino-group, giving 5-nitro-*o*-4-xylidine (VI), since by means of the diazo-



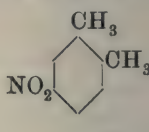
(IV.)



(V.)



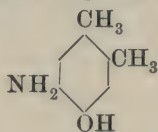
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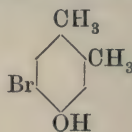
(VII.)

reaction the amino-group can be replaced by a hydrogen atom, and there results 4-nitro-*o*-xylene (VII) (Jacobson, *Ber.*, 1884, **17**, 160).

5-Nitro-*o*-4-xylanol was then reduced by means of sodium hyposulphite, and the resulting 5-amino-*o*-4-xylanol (VIII) diazotised and treated with cuprous bromide, but the 5-bromo-*o*-4-xylanol (IX)



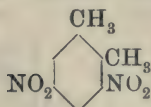
(VIII.)



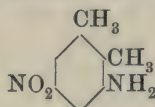
(IX.)

so prepared melted at 80°, and was not therefore the desired bromoxylanol.

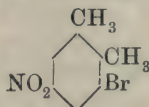
In the next place, 6-bromo-*o*-4-xylanol (III) was made in the following manner. 3:5-(4:6-)Dinitro-*o*-xylene (X) (T., 1909, **95**, 209) was converted into 5-nitro-*o*-3-xylidine (XI), as already described (T., 1911, **99**, 2351). In this substance the amino-group was replaced by bromine and the resulting bromonitro-*o*-xylene



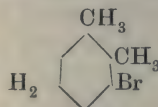
(X.)



(XI.)



(XII.)



(XIII.)

(XII) reduced to 6-bromo-*o*-4-xylidine (XIII), in which substance the amino-group was replaced by hydroxyl, thus giving rise to

3-bromo-*o*-5-xylenol or 6-bromo-*o*-4-xylenol (III), which melted at 103°, and was identical with the bromoxylenol of the same melting point obtained by the action of heat on dibromodimethylcyclohexenone.

EXPERIMENTAL.

5-Amino-o-4-xylenol.

o-4-Xylenol was nitrated according to the directions of Diepolder (*Ber.*, 1909, **42**, 2916), and the crude product distilled in steam and then crystallised from alcohol, by which means a fairly easy separation of the mono- and dinitro-*o*-xylenols, both of which are produced in the reaction, can be accomplished. Twenty-five grams of *o*-4-xylenol gave 12.2 grams of 5-nitro-*o*-4-xylenol, 3.1 grams of 3:5-dinitro-*o*-4-xylenol, and 3.8 grams of fractions of intermediate melting point.

Two grams of 5-nitro-*o*-4-xylenol were dissolved in 100 c.c. of alcohol, the solution made alkaline by the addition of sodium hydroxide solution, heated on a water-bath, and a saturated solution of sodium hyposulphite gradually added until the whole became colourless (compare Grandmougin, *Ber.*, 1906, **39**, 2494). On evaporating the alcohol, an almost quantitative amount of 5-amino-*o*-4-xylenol separated, which, after one crystallisation from alcohol, melted at 173—175° (Diepolder, *loc. cit.*, p. 2920). A similar result was obtained by carrying out the reduction without the addition of sodium hydroxide.

A simpler method for preparing 5-amino-*o*-4-xylenol is by the reduction of 1:2-dimethyl-4:5-benzoquinonephenylhydrazone with sodium hyposulphite as described by Diepolder (*Ber.*, 1911, **44**, 2498).

5-Bromo-o-4-xylenol.

Six grams of the aminoxylenol were dissolved in 50 c.c. of water, and 12 grams of 40 per cent. hydrobromic acid, diazotised with 20 per cent. sodium nitrite at 0°, poured into a solution of 3 grams of cuprous bromide in 15 c.c. of 40 per cent. hydrobromic acid, and the whole, after standing two hours, steam distilled. The distillate, on filtration, gave 4.5 grams of a white solid, which, after crystallisation from light petroleum, was analysed:

0.1195 gave 0.1124 AgBr. Br = 40.02.

C₈H₉OBr requires Br = 39.80 per cent.

5-Bromo-o-4-xylenol is very soluble in the cold in the ordinary organic solvents, and crystallises from light petroleum (b. p. 40—60°) in bunches of glistening needles, melting at 80°.

The *benzoyl* derivative, prepared in the usual manner, is very

soluble in the cold in light petroleum, acetone, chloroform, ethyl acetate, or benzene, and crystallises from alcohol in transparent plates, melting at 51° :

0.1381 gave 0.0864 AgBr. $\text{Br} = 26.62$.

$\text{C}_{15}\text{H}_{13}\text{O}_2\text{Br}$ requires $\text{Br} = 26.23$ per cent.

The *o*-nitrobenzoyl derivative is readily soluble in the cold in acetone or chloroform, less readily in ethyl acetate or benzene, not at all readily soluble in alcohol or light petroleum, and crystallises from ethyl acetate in transparent, rectangular plates, melting at $151\text{--}152^{\circ}$:

0.2698 gave 9.2 c.c. N_2 (moist) at 17° and 756 mm. $\text{N} = 3.93$.

$\text{C}_{15}\text{H}_{12}\text{O}_4\text{BrN}$ requires $\text{N} = 4.00$ per cent.

Preparation of 6-Bromo-o-4-xyleneol.

5-Nitro-*o*-3-tylidine (T., 1911, **99**, 2351), in quantities of 5 grams at one time, was suspended in 40 c.c. of water, together with 10 grams of 40 per cent. hydrobromic acid, and treated with 20 per cent. sodium nitrite solution at 0° . The clear solution was poured into 2 grams of cuprous bromide dissolved in 10 grams of 40 per cent. hydrobromic acid, maintained at $30\text{--}35^{\circ}$, allowed to stand for two hours and steam distilled. The solid passing over with the steam amounted to 5.4 grams, and after crystallisation from alcohol it was analysed:

0.2151 gave 11.5 c.c. N_2 (moist) at 16° and 757 mm. $\text{N} = 6.20$.

$\text{C}_8\text{H}_8\text{O}_2\text{NBr}$ requires $\text{N} = 6.09$ per cent.

3-Bromo-5-nitro-*o*-xylene is readily soluble in the cold in chloroform, ethyl acetate or benzene, readily soluble in acetone or alcohol on warming, and crystallises from the latter solvent in long, colourless, glistening needles, melting at 101° .

Twelve grams of bromonitro-*o*-xylene were finely powdered, suspended in 90 c.c. of alcohol, and a solution of 47 grams of stannous chloride in 90 grams of concentrated hydrochloric acid gradually added. The whole was allowed to stand, and the reaction then completed by slight warming on the water-bath. On making alkaline and steam distilling, 9.8 grams of a colourless solid passed over, which was purified by crystallisation from dilute alcohol:

0.2840 gave 17.6 c.c. N_2 (moist) at 18° and 757 mm. $\text{N} = 7.12$.

$\text{C}_8\text{H}_{10}\text{NBr}$ requires $\text{N} = 7.00$ per cent.

6-Bromo-*o*-4-tylidine is readily soluble in the ordinary organic solvents (except light petroleum) in the cold, and crystallises from dilute alcohol in masses of fine, silken needles, melting at 82° .

The *monoacetyl* derivative, prepared by heating the amine with acetyl chloride, is fairly soluble in the cold in chloroform, ethyl

acetate, or acetone, and crystallises from alcohol in small, transparent plates, melting at 205—206°:

0.2512 gave 12.3 c.c. N_2 (moist) at 14° and 750 mm. $N=5.68$.

$C_{10}H_{12}ONBr$ requires $N=5.78$ per cent.

Acetic anhydride was used in the first preparation of the acetyl derivative, when it was found that the main portion of the product melted at 109°, and proved to be the *diacetyl* derivative of the amine. It can also be obtained by heating the monoacetyl derivative with acetic anhydride for two hours, when it crystallises from alcohol in transparent, four-sided plates, melting at 109°:

0.2554 gave 10.6 c.c. N_2 (moist) at 17° and 762 mm. $N=4.83$.

$C_{12}H_{14}O_2NBr$ requires $N=4.93$ per cent.

A determination of the acetyl value was made by hydrolysing with alcoholic potassium hydroxide, evaporating the alcohol, acidifying with sulphuric acid, and distilling the acetic acid in a current of steam:

0.3322 required 23 c.c. $N/10$ -KOH. $CH_3 \cdot CO=29.77$.

$C_8H_8NBr(CH_3 \cdot CO)_2$ requires $CH_3 \cdot CO=30.28$ per cent.

Five grams of 6-bromo-o-4-xyldine in 90 c.c. of 40 per cent. sulphuric acid were diazotised with a 20 per cent. solution of sodium nitrite at 50—60°, poured into 150 c.c. 40 per cent. sulphuric acid, heated on the water-bath, steam distilled, and the resulting solid (2.9 grams) crystallised from light petroleum:

0.1173 gave 0.1110 AgBr. $Br=40.21$.

C_8H_9OBr requires $Br=39.80$ per cent.

3-Bromo-o-5-xylenol (6-bromo-o-4-xylenol) is readily soluble in the cold in alcohol, ethyl acetate, acetone, or chloroform, less readily so in benzene, and crystallises from light petroleum (b. p. 80—100°) in masses of silken needles, melting at 103°.

When treated with bromine in chloroform solution, it gives tribromo-o-4-xylenol, melting at 172—173°.

The *benzoyl* derivative is readily soluble in acetone, ethyl acetate, chloroform, or benzene, and crystallises from methyl alcohol in transparent, glistening, six-sided plates, melting at 85°:

0.1385 gave 0.0862 AgBr. $Br=26.48$.

$C_{15}H_{13}O_2Br$ requires $Br=26.23$ per cent.

The *o-nitrobenzoyl* derivative crystallises from ethyl acetate in almost colourless, glistening needles, or on slow crystallisation in stout, transparent prisms, melting at 132°:

0.2945 gave 10.0 c.c. N_2 (moist) at 15° and 758 mm. $N=3.97$.

$C_{15}H_{12}O_4NBr$ requires $N=4.00$ per cent.

CXXXVIII.—*The Refractivities of Acenaphthene and its Monohalogen Derivatives.*

By HOLLAND CROMPTON and WILHELMINA REBECCA SMYTH.

UP to the present the refractivities of compounds containing the acenaphthene ring have not been determined. This, no doubt, is due to the fact that most of these compounds are of high melting point, and therefore not easy to deal with in the liquid state. This difficulty does not arise with the monohalogen derivatives of acenaphthene, which have been described by one of us and Miss M. Walker (T., 1912, **101**, 958), as these compounds melt at a sufficiently low temperature to make their examination a comparatively easy matter. We have therefore prepared pure specimens of these compounds, and measured their refractive indices. For the purpose of comparison, acenaphthene has also been examined. The measurements were made with a Zeiss-Pulfrich refractometer, heated either with hot water or steam. Readings could be easily obtained for the C- and F-hydrogen lines, and for the D-sodium line. The molecular refractions were calculated with the Lorenz-Lorentz formula, the densities used in the case of the halogen derivatives of acenaphthene being those determined by Crompton and Walker (*loc. cit.*).

Acenaphthene, C₁₂H₁₀.

Kahlbaum's acenaphthene was purified by distillation and crystallisation from alcohol. The specimen taken for examination melted in a capillary tube at 95°. Owing to the high melting point, determinations could only be made with the refractometer heated by steam, the temperature then registered being 98·8°. The refractive indices measured at this temperature were:

$$n_C = 1.59772; n_D = 1.60482; n_F = 1.62705.$$

The density of acenaphthene at 98·8°, taken from the determinations of R. Schiff (*Annalen*, 1884, **223**, 262), is 1.0331. The molecular refractions of acenaphthene are therefore:

$$M_C = 50.84; M_D = 51.33; M_F = 52.84.$$

This gives the molecular dispersion $M_F - M_C = 2.00$.

The molecular refraction, M_C , of naphthalene determined at 98·4° by Brühl (*Zeitsch. physikal. Chem.*, 1887, **1**, 307) is 43.93. Taking the values given by Eisenlohr (*Zeitsch. physikal. Chem.*, 1910, **75**, 585) for the atomic refraction of carbon, 2.413, and of hydrogen, 1.092, for the C-line, the molecular refraction of

acenaphthene, calculated from that of naphthalene, is $M_C = 50.94$, which agrees fairly with the observed value.

3-Chloroacenaphthene, $C_{12}H_9Cl$.

The refractive indices were determined at the following temperatures:

t° .	n_C .	n_D .	n_F .
71.4	1.62156	1.62875	1.64988
72.7	1.62131	1.62850	1.64950
77.1	1.61933	1.62631	1.64747
85.37	1.61624	1.62284	1.64413
99.75	1.61048	1.61685	1.63817

As, within these limits, the refractive index varies regularly with the temperature, the values for 69.8° were obtained by extrapolation, and with the density of chloroacenaphthene determined at this temperature, 1.1955, the molecular refractions were then calculated as follows:

$$M_C = 55.53; M_D = 56.07; M_F = 57.55.$$

The molecular dispersion is $M_F - M_C = 2.02$.

With Eisenlohr's value for the atomic refraction of chlorine, 5.933, the molecular refraction of chloroacenaphthene calculated from that of acenaphthene is $M_C = 55.68$.

3-Bromoacenaphthene, $C_{12}H_9Br$.

Determinations were made at the following temperatures:

t° .	n_C .	n_D .	n_F .
54.3	1.64796	1.65651	1.67943
64.7	1.64373	1.65207	1.67564
69.8	1.64142	1.65013	1.67317
83.0	1.63586	1.64433	1.66730
99.55	1.62888	1.63794	1.66016

The refractive index, as in the case of chloroacenaphthene, varies regularly with the temperature. The density of bromoacenaphthene has been determined at 51.2° , at which temperature it has the value 1.4397, and on obtaining the refractive indices at that temperature by extrapolation, the following molecular refractions were calculated:

$$M_C = 58.97; M_D = 59.58; M_F = 61.22.$$

This gives the molecular dispersion $M_F - M_C = 2.25$.

Eisenlohr's value for the atomic refraction of bromine is 8.803, and with this the molecular refraction of bromoacenaphthene calculated from that of acenaphthene is $M_C = 58.55$.

3-Iodoacenaphthene, C₁₂H₉I.

Owing to the slight colour which this compound develops on heating, readings were not so easily obtained in this case as with the previous compounds. The values given below are from two independent sets of observations, the results of which are in fair agreement.

t° .	n_D .	n_D .	n_F .
65.5	1.68117	1.69085	1.71767
66.3	1.68089	—	1.71762
75.18	1.67667	1.68641	1.71805
80.4	1.67440	1.68390	—
80.8	1.67430	1.68379	1.71057
98.85	1.66665	1.67619	1.70246

From these values the refractive indices at 62° were obtained as before by extrapolation. The density of iodoacenaphthene at this temperature is 1.6738, and the calculated values for the molecular refractions are therefore as follows:

$$M_C = 63.42; M_D = 64.10; M_F = 66.02.$$

This gives the molecular dispersion $M_F - M_C = 2.60$.

The atomic refraction of iodine is given by Eisenlohr as 13.757. With this value the molecular refraction of iodoacenaphthene calculated from that of acenaphthene is $M_C = 63.50$.

The general agreement between the observed and the calculated values for the refractions of acenaphthene and its monohalogen derivatives shows that there is nothing abnormal in the optical behaviour of these compounds. Although in the production of acenaphthene from naphthalene a five-carbon-atom ring is formed, this has no perceptible influence on the refraction, the case fully resembling that of *cyclopentane*, which is also optically normal (see Eisenlohr, *Spectrochemie organischer Verbindungen*, p. 86).

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CXXXIX.—Dibenzoyldiaminoacetic Acid.

By PAUL HAAS.

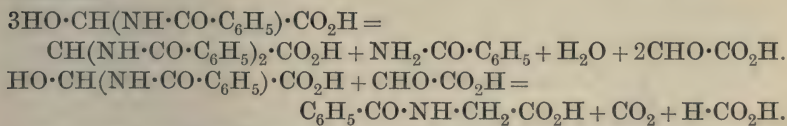
IN a previous communication (T., 1912, **101**, 1254) it was stated that α -hydroxyhippuric acid, when heated in a capillary tube, softens and melts with frothing at 145—150° and then resolidifies, but that on further heating it darkens at about 180°, and finally melts and decomposes at 208—210°.

With the object of investigating the change undergone by the substance, 3 grams of it were heated in a distillation flask immersed

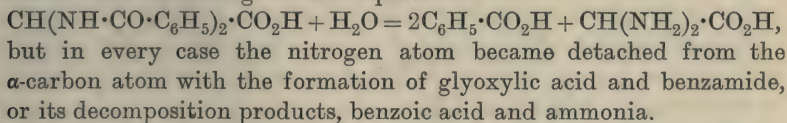
in a metal-bath at 150—160° for a quarter of an hour. The substance became pasty, and evolved some carbon dioxide, and at the same time a little formic acid distilled over, together with a small quantity of a crystalline solid, which proved to be benzamide. Subsequently it was found more convenient to heat about 10 grams at a time in an open porcelain vessel, as the substance could then be stirred during the process. After heating for a quarter of an hour, the buff-coloured residue, weighing 7.5 grams, was extracted repeatedly with hot water until the aqueous extracts (A) were colourless; the remaining solid, which weighed about 4 grams, was crystallised from glacial acetic acid, and on analysis was found to be the dibenzoyl derivative of diaminoacetic acid.

The strongly acid aqueous extracts (A) were shown to contain free glyoxylic acid, since on distillation they yielded an acid distillate, which gave Hopkins' reaction with peptone solution and concentrated sulphuric acid. From the same extract there were also obtained on evaporation small quantities of benzamide and of hippuric acid.

The formation of all these substances may be represented by the following equations, which, as it happens, also represent approximately the proportions in which these substances are actually obtained:



Repeated attempts were made to hydrolyse the dibenzoyldiaminoacetic acid according to the equation:



Dibenzoyldiaminoacetic acid, $\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5)_2\cdot\text{CO}_2\text{H}$, obtained by heating α -hydroxyhippuric acid in the manner described above, is a buff-coloured solid, which, when crystallised from glacial acetic acid, separates in colourless, glistening needles, and melts at 234° (Found, C=64.30; H=4.92; N=9.50. Calc., C=64.43; H=4.69; N=9.39 per cent.). The substance is sparingly soluble in boiling acetic acid or alcohol, and is very sparingly so in boiling water or acetone, but is practically insoluble in most other organic solvents; its constitution may be regarded as established by the fact that a substance of the same composition and melting point was obtained by Einhorn and Ladisch (*Annalen*, 1906, **343**, 227) by heating together benzamide and glyoxylic acid. As these authors did not prepare

a single derivative of their acid, it was thought desirable to characterise the substance more fully as follows.

A molecular-weight determination by titration gave the following numbers:|

0.1286 required for neutralisation 4.95 c.c. *N*/10-KOH. M.W. = 297.

$C_{16}H_{14}O_4N_2$ requires M.W. = 298.

The *silver* salt is formed as a white, crystalline precipitate on mixing together aqueous solutions of the sodium salt and silver nitrate:

0.1804 gave 0.3130 CO_2 and 0.0565 H_2O . C = 47.33; H = 3.48.

0.2164 „ 13.8 N_2 (moist) at 15.5° and 751 mm. N = 7.19.

0.1542 „ 0.0410 Ag. Ag = 26.58.

$C_{16}H_{13}O_4N_2Ag$ requires C = 47.41; H = 3.21; N = 6.91;
Ag = 26.66 per cent.

The *calcium* salt separates from solution as a white, crystalline precipitate:

0.4014 gave 0.0358 CaO. Ca = 6.36.

$(C_{16}H_{13}O_4N_2)_2Ca$ requires Ca = 6.17 per cent.

The *ammonium* salt was prepared by dissolving the acid in ammonium hydroxide and evaporating the solution to dryness; it is soluble in water or alcohol, and crystallises from a mixture of alcohol and light petroleum in glistening silken needles, melting and decomposing at $200-203^\circ$:

0.1222, by Kjeldahl's method, required 11.1 c.c. *N*/10-HCl.
N = 12.72.

$C_{16}H_{17}O_4N_3$ requires N = 13.33 per cent.

The *methyl* ester, prepared by heating the silver salt with methyl iodide in dry benzene, melts at $224-225^\circ$; it is fairly soluble in boiling chloroform, and separates from a mixture of this solvent with acetone in aggregates of silken needles; it is sparingly soluble in most organic solvents:

0.1862, by Kjeldahl's method, required 12.4 c.c. *N*/10-HCl.
N = 9.32.

$C_{17}H_{16}O_4N_2$ requires N = 8.97 per cent.

The *ethyl* ester was obtained while attempting to hydrolyse the acid by treating it with a saturated alcoholic solution of hydrogen chloride for three hours at 130° . The resulting crystalline solid was purified by recrystallisation from glacial acetic acid, from which it separated in square plates:

0.1126 gave 0.2733 CO_2 and 0.0606 H_2O . C = 65.95; H = 5.98.

$C_{18}H_{18}O_4N_2$ requires C = 66.25; H = 5.52 per cent.

It is soluble in hot alcohol or acetone, but is only sparingly soluble in chloroform or benzene, and melts at $205-207^\circ$.

Hydrolysis of Dibenzoyldiaminoacetic Acid.

Having thus definitely established the existence of dibenzoyldiaminoacetic acid as a perfectly stable, crystalline solid, the question of the existence of the monobenzoyldiaminoacetic acid described by Drechsel acquired renewed interest. According to this author, the monobenzoyl derivative of diaminoacetic acid is a crystalline solid, melting at 227° , which on hydrolysis with alcoholic hydrogen chloride yielded the hydrochloride of diaminoacetic acid. From the observations of other authors, however, it seemed unlikely that the substances described by Drechsel actually had the constitutions which he assigned to them, and so the existence of the monobenzoyl derivative of diaminoacetic acid has been denied.

In so far as the present investigation can throw any light on this question, it may be stated that the stability and the melting point of the dibenzoyl derivative here described would lend support to the existence of a stable monobenzoyl derivative, melting at 227° ; as regards their behaviour on hydrolysis, however, there would appear to be a considerable difference in properties between the two substances, inasmuch as Drechsel's compound was apparently readily converted into diaminoacetic acid, whereas all attempts to hydrolyse dibenzoyldiaminoacetic acid either under conditions similar to those employed by Drechsel, or under entirely different conditions, resulted, as already stated, in the formation of glyoxylic acid and benzamide or its decomposition products.

The following experiment under conditions closely resembling those given by Drechsel may be quoted. Two grams of dibenzoyldiaminoacetic acid were heated in a sealed tube with 8 c.c. of a mixture of equal parts of concentrated hydrochloric acid and ethyl alcohol for two hours at 140° . The contents of the tube consisted of an aqueous solution with an oil floating on its surface. The aqueous layer contained glyoxylic acid and ammonium chloride, whilst the oily layer consisted of ethyl benzoate, together with a small quantity of ethyl dibenzoyldiaminoacetate.

Attempts to hydrolyse the acid by heating it with absolute alcohol saturated with hydrogen chloride or by heating it with dilute hydrochloric acid or with aqueous potassium hydroxide likewise failed to give any diaminoacetic acid.

The author is indebted to the Research Fund Committee for a grant which has, in part, defrayed the cost of this investigation.

CXL.—*Keto-enolic Tautomerism and the Absorption Spectra of the Aliphatic Ketones.*

By HARRY MEDFORTH DAWSON.

FROM an examination of the ultra-violet absorption spectra of certain keto-enol tautomerides, Baly and Desch (T., 1904, **85**, 1029; 1905, **87**, 766) were led to suppose that the intramolecular change of linking which occurs when one isomeric form is transformed into the other according to the equation $\cdot\text{CH}_2\cdot\text{CO}\cdot \rightleftharpoons \cdot\text{CH}:\text{C}(\text{OH})\cdot$ is associated with the selective absorption of rays of short wave-length. Observations relating to the simple ketones were described somewhat later by Stewart and Baly (T., 1906, **89**, 489), which were considered to support this theory. The aliphatic ketones were found to exhibit a more or less well-defined absorption band similar to that shown by the 1:3-diketones and ketonic esters, and it was claimed that the persistence of this band is definitely related to the reactivity of the carbonyl group.

If the chemical reactivity is regarded as a direct result of the intramolecular change of linking, and the ultra-violet absorption is attributed to the resonance of the electronic constituents of the atoms which are more or less directly concerned, the electrons being caused to vibrate with a more or less definite frequency as a result of intramolecular atomic change, there does not appear to be any serious objection on physical grounds to an attempt to correlate the chemical reactivity and the absorption spectrum in the manner suggested.

In view of the wide dissemination of the views of Baly and Desch, and of the importance of the alleged connexion between the reactivity of the simple aliphatic ketones and the intensity of the ultra-violet absorption, it seems to be a matter of some importance to examine the facts more closely than has been done previously.

In what follows it will be shown: first, that the reactivity of the carbonyl group, as measured by the bisulphite and hydroxylamine reactions, has no connexion with the rate of isomeric change; secondly, that the only way in which the selective absorption bands of the members of a group of similar substances can be compared is by reference to the extinction-coefficients for light of that frequency which is regarded as characteristic of the group; thirdly, that the rates of isomeric change of the simple aliphatic ketones are not related to the extinction-coefficients for light of the frequency which is supposed to be characteristic of the $\cdot\text{CH}_2\cdot\text{CO}\cdot$ group; and fourthly, that an increase in the rate of isomeric change of the

simplest ketone in the ratio of about 100,000 : 1 has no appreciable influence on the extinction-coefficient.

Reactivity of the Carbonyl Group and the Rate of Isomeric Change in the Aliphatic Ketones.

As a measure of the reactivity of the $\cdot\text{CH}_2\cdot\text{CO}\cdot$ group, Baly and Stewart made use of the data obtained by Stewart in experiments with the ketones, in which the rate of addition of sodium hydrogen sulphite (T., 1905, **87**, 185) and of oxime formation (*ibid.*, p. 410) were examined. If these data are scrutinised, it is, however, quite clear that comparable numbers cannot be derived from the data for either of these reactions. This is at once evident from the curves which are obtained by plotting the percentage of ketone which has been converted into the bisulphite compound or the oxime against time; it cannot even be asserted that the curves are of the same type. Comparative numbers would no doubt be afforded by the velocity-coefficients, or, in the case of practically non-reversible changes, by the actually observed velocities for corresponding fractions of the complete reaction, but such data are not available either for the bisulphite or the oxime reaction. Both reactions are reversible, and in the case of certain ketones, the experimental data indicate that the equilibrium condition has been practically reached either before or during the period covered by the observations. In these cases, the experimental numbers might be utilised for the calculation of the dissociation constants of the bisulphite compounds or oximes, but not for the deduction of comparable reaction-velocities. The observations do not, in fact, suffice to show the kinetic nature of the change in the case of either the bisulphite or oxime reaction. In these circumstances, the data obtained by Stewart cannot be regarded as affording even an approximate measure of the relative reactivities of the $\cdot\text{CH}_2\cdot\text{CO}\cdot$ group in the different ketones.

The only data at present available which afford a quantitative comparison of the relative reactivities of the aliphatic ketones are to be found in the observations which have been made on the rate of action of the halogens on the ketones in dilute aqueous alcoholic solution in presence of an acid catalyst (Dawson and Wheatley, T., 1910, **97**, 2048; Dawson and Ark, T., 1911, **99**, 1740). The fact that the velocity of this reaction is independent of the nature and concentration of the halogen indicates with great probability that the velocity in question is determined by the speed of the preliminary isomeric change, in which the group $\cdot\text{CH}_2\cdot\text{CO}\cdot$ is transformed into $\cdot\text{CH}:\text{C}(\text{OH})\cdot$. In presence of excess of ketone, the reaction progresses at a constant speed, and the actually

observed velocities for the different ketones, when these are examined under the same conditions, are directly proportional to the velocity-coefficients for the isomeric change in question.

In the following table are given the data for a number of ketones, in which the effect of the replacement of hydrogen by a methyl group is evident. The numbers under I and II are taken from Stewart's papers (*loc. cit.*), and represent respectively the fraction of ketone converted into the bisulphite compound (after forty minutes) and the fraction converted into oxime (after twenty minutes), whilst those under III represent the relative speeds of isomeric change (acetone=1) as measured by the rate at which iodine disappears from the corresponding solutions of the ketones.

	I.	II.	III.
Acetaldehyde.....	0·887	—	(0·04)*
Acetone	0·536	0·497	1·00
Methyl ethyl ketone.....	0·291	0·392	1·042
Methyl propyl ketone ...	0·184	0·373	0·937
Methyl <i>isopropyl</i> ketone.	0·094	0·315	0·695
Pinacolin.....	0·056	0·170	0·458

From this table it is apparent that the position of acetaldehyde is absolutely different according to whether the data in I or III are compared. Apart from this discrepancy, it cannot be denied that the three series of numbers in the table exhibit a certain parallelism, but for reasons which have been already stated at some length, it is quite certain that this is of a more or less accidental character. If the ketones are to be compared in respect of their reactivities, the only available numbers are, in fact, those recorded in the third column of the table.

That the "velocity" data for the bisulphite and oxime reactions have no connexion with the speed of the isomeric change is, moreover, very evident when the absolute velocities of the reactions are considered. From Stewart's data (*loc. cit.*) for the quantity of ketone which is transformed during the initial period of observation, it appears that the amount of acetone which reacts with sodium bisulphite or with hydroxylamine sulphate is of the order of $1 \cdot 10^{-3}$ mols. per litre per minute (temperature = 0° , acetone concentration = $1/24$ molar).

From observations on the auto-catalytic reaction between acetone and iodine (Dawson and Powis, T., 1912, 101, 1503), it can be shown that in neutral solution and at the same temperature and acetone concentration, the quantity of acetone which changes from the ketonic to the enolic form is roughly $1 \cdot 10^{-10}$ mols. per litre per minute. From this it follows that the rate of reaction of acetone

* The number given for acetaldehyde is only approximate, and has been estimated from data obtained in experiments with acetaldehyde which are now in progress.

with sodium hydrogen sulphite or with hydroxylamine is about ten million times greater than the rate of isomeric change as measured by the rate at which iodine would disappear from a "neutral" aqueous solution of acetone. This enormous difference between the reaction-velocities indicates that the bisulphite and oxime reactions are in no way related to the tautomeric change, and that reactivities measured by reference to these reactions cannot be supposed to have any connexion with the relative frequencies of the intramolecular change of linking in the $\cdot\text{CH}_2\cdot\text{CO}\cdot$ group.

Ultra-violet Absorption Spectra of the Ketones: Method of Comparing the Selective Absorption Capacities.

From what has been stated in the previous section, it is evident that the bisulphite and oxime reactions cannot legitimately be employed in any attempt to correlate the intensity of the selective absorption with the frequency with which the keto-enolic transformation occurs in the different ketones. For this purpose reference must be made to the relative-velocities of isomeric change as measured by the rates at which the ketones react with the halogens.

Before the question of the existence of such a connexion can be dealt with in any satisfactory way, it will be necessary to consider the method to be adopted in comparing the selective absorption produced by the individual members of a group of similar substances, all of which give rise to absorption in the same spectral region. The same problem is, of course, involved in the comparison of the absorption produced by one and the same substance under different conditions, as, for example, when the substance is dissolved in different solvents, or when foreign substances are added to the solution of the substance in a particular solvent.

It would appear that the method adopted by most observers is to compare the so-called persistencies of the absorption band. The persistence is measured by the difference between the thicknesses of those layers of a standard solution of the active substance which correspond respectively with the initial appearance and the final disappearance of the selective band. According to the views of Baly and Desch, the persistence of this band in the case of the aliphatic ketones would afford a measure of the rate of the keto-enolic transformation, that is to say, of the number of molecules which are actually in the transitory condition at any moment.

Quite apart from any such special theory, it is, however, extremely improbable that the persistence of a selective absorption band has any definite physical significance. The commencement of the band corresponds merely with that thickness of absorbing layer

at which the selective absorption begins to be differentiated from the general absorption, and the disappearance of the band with that thickness for which the absorbing layer of solution produces no appreciable effect on a particular type of photographic plate during a definite period of exposure. If the source of light, the sensitiveness of the photographic plate, and the time of exposure are kept constant, it is no doubt quite possible, on the other hand, to attach definite significance to the numbers which express the relative thicknesses of those layers of the different solutions for which the absorption band seems just to disappear. In other words, it is suggested that the comparison between the absorption produced by equivalent solutions of one and the same substance or of a series of closely similar substances should be made by reference to those thicknesses of the absorbing layers which correspond with the head of the extinction curve, and that no special significance can be attached to the persistence of a selective absorption band as measured in the usual way. The theoretical argument in favour of this method of comparing absorption spectra may now be put forward.

Whatever the mechanism of ultra-violet absorption, whether it is determined by a particular condition of the molecules of the substance or by some form of intra-molecular change, then so long as the incidence of such condition or intramolecular change is regulated by the law of probability and does not involve the interaction of two or more molecules, it may be inferred that the absorption of light by the dissolved substance will be determined by the number of molecules which are in the active condition. If the substance itself is inactive, but gives rise to selective absorption of definite wave-length on the addition of a foreign substance with which it enters into combination, the intensity of the absorption will similarly be determined by the number of molecules of the active compound which are formed. In these circumstances, the relative change in intensity (I) of a beam of light which has passed through a layer of solution of thickness dx will be given by:

$$-dI/I = k \cdot dx,$$

where the absorption coefficient k affords a measure of the number of molecules which are in the active condition.

On integration, it is found that the intensity of the light, I_x , which is transmitted by a layer of a standard solution of thickness x , is given by:

$$I_x = I_0 e^{-kx},$$

in which I_0 is the intensity of the incident beam. For convenience this may be written in the form:

$$kx = \log I_0 - \log I_x.$$

If the same constant source of light is used in all the experiments which belong to the series required, I_0 may be regarded as constant. Similarly, if I_x is the intensity of the transmitted light, which in a definite and fixed time interval is just sufficient to produce a perceptible impression on the photographic plates used, then I_x may be also regarded as constant.

If, further, for two equimolar solutions of the same or similar substances, the values of k are k_1 and k_2 , and the thicknesses of the layers of these solutions, which, in the same time interval, give rise to an impression on the photographic plate which is just perceptible, are x_1 and x_2 respectively, we shall have the relation:

$$k_1 x_1 = k_2 x_2,$$

$$\text{or } k_1/k_2 = x_2/x_1.$$

Since now k is a measure of the frequency with which the molecules enter into that condition in which they absorb ultra-violet light of a certain wave-length, it follows that the relative thicknesses of those layers which give rise to the same amount of absorption will vary inversely as the number of molecules which are in the active condition at a particular moment. Since the fraction of the total molecules which are in the active condition remains unchanged, it follows that the thicknesses of the layers in question will be in the inverse ratio of the number of active molecules of the substance or substances which are present in the different solutions.

In regard to the actual method of obtaining the relative thicknesses of the layers of equivalent solutions which have the same absorbing power for the selectively absorbed light, there can be little doubt that the best results would be obtained by the use of a spectro-photometer. It might also be possible to obtain fairly accurate data photographically by a suitable modification of the null method described by Merton (this vol., p. 124). A less accurate method, but one which for many purposes may give all the information that is required, is afforded by the comparison of the ordinary photographic data in the form of the extinction curves. All that is necessary is to estimate the thicknesses of the various solutions which correspond with the head of the respective extinction curves.

In the following section, this method of comparison will be applied to the extinction curves of the aliphatic ketones.

Absorption-coefficient and the Rate of Isomeric Change in the Aliphatic Ketones.

According to the fundamental idea underlying the Baly-Desch theory, the intensity of the ultra-violet absorption of the aliphatic

ketones ought to be proportional to the absorption-coefficient, for the reversible isomeric change is unimolecular, and the rate at which it occurs is therefore independent of the volume occupied by the substance. In these circumstances, the absorption-coefficient affords a measure of the frequency with which the change takes place which is supposed to be responsible for the selective absorption. The thicknesses of layers of equimolar solutions of the various ketones which correspond with the disappearance of the absorption band should therefore be in the inverse ratio of the rates of isomeric change.

If the extinction curves for the aliphatic ketones investigated by Stewart and Baly (*loc. cit.*, p. 492) are examined in reference to this theoretical deduction, it will be found that there is no agreement whatever. Although the thicknesses of the layers of the different solutions which correspond with the disappearance of the absorption band cannot be estimated very accurately from these curves, it is quite clear that these thicknesses are approximately the same for acetone, methyl ethyl ketone, methyl propyl ketone, methyl isopropyl ketone, pinacolin, and methyl hexyl ketone. On the other hand, by reference to the numbers in the third column of the table on p. 1310, it will be found that there are considerable differences between the reactivities of some members of this series. The conclusion to be drawn from this is that there is no connexion between the ultra-violet absorption of the aliphatic ketones and the rate of isomeric change as measured by the reactivity towards the halogens.

From observations on the absorption spectra of camphor derivatives, Lowry and Desch (*T.*, 1909, **95**, 807) have already shown that the selective absorption characteristic of these substances has no connexion with the transfer of a labile hydrogen atom, and that the persistence of the band cannot be regarded as a measure of the frequency of the intramolecular transformation which occurs during the actual conversion of one isodynamic form into the other. From a detailed investigation of the absorption spectrum of ethyl acetoacetate under different conditions, Hantzsch (*Ber.*, 1910, **43**, 3049) has also thrown grave doubt on the views put forward by Baly and his co-workers, and at the same time has adduced evidence in support of the view that substances containing the group $\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot$ owe their selective absorption to a particular static molecular configuration. A similar conclusion was arrived at by Lowry and Desch in their interpretation of the spectral behaviour of camphor compounds.

In spite of this cumulative evidence,* a very special interest

* Compare also Purvis and McClelland, *T.*, 1912, **101**, 1810.

necessarily attaches to the case of the monoketones, and in particular to acetone and its homologues. This is not only due to the fact that these are the simplest substances which contain the $\cdot\text{CH}_2\cdot\text{CO}\cdot$ group, but also to the fact that no data are available for the diketones which afford a measure of their rates of isomeric change under different conditions. It is quite true that the experiments of Lowry and Desch on the behaviour of nitrocamphor and of β - and π -bromonitrocamphor in different solvents afford conclusive evidence that the spectral behaviour of these substances is quite independent of the rate of isodynamic change, but it may be doubted whether the isodynamic change in question is of the simple keto-enol type.

Certain experiments, which the author has had in view for some time, but which it has not been possible to carry out for lack of some of the necessary apparatus, are now rendered unnecessary by reason of the fact that the requisite absorption data are furnished by the recent work of Brannigan, Macbeth, and Stewart (this vol., p. 406). According to these observers, the absorption curve for a pure aqueous solution of acetone is not sensibly different from the curve for a solution of acetone in *N*-hydrochloric acid.

According to the results obtained by the author and Powis in the investigation of the auto-catalytic reaction between acetone and iodine (*loc. cit.*), it would appear that the rate of isomeric change of acetone in pure aqueous solution is not greater than that which would correspond with the catalytic action of 0.00002*N*-hydrochloric acid. From direct observations of the rate of change under the influence of hydrochloric acid at small concentrations, it has been further shown that the velocity (v) at 25° for a solution containing 20 c.c. of acetone per litre is given by $v = 4.50 \times n \times 10^{-4}$ mols. per litre per minute, where n is the molar concentration of the catalysing acid. In *N*-hydrochloric acid solution, the observed rate of change under similar conditions is $v = 5.15 \times 10^{-4}$ mols. per litre per minute.

From these data it is possible to compare the rates of isomeric change of acetone in pure aqueous solution and in *N*-hydrochloric acid. The ratio of these velocities may then be compared with that of the absorption-coefficients, this ratio being deducible from the curves recorded by Stewart and his collaborators (*loc. cit.*, p. 417). The logarithms of the thicknesses of a *N*/100,000-solution of acetone in water and in *N*-hydrochloric acid, which correspond with the head of the selective absorption band ($1/\lambda = 3800$), are respectively 5.38 and 5.25. In other words, the thicknesses of layers of *N*/10-solutions of acetone which absorb ultra-violet light of this frequency to the same extent are respectively 24 and 18 mm. We

have therefore the following relations between the rates of isomeric change and the ultra-violet absorption capacities in neutral aqueous and *N*-hydrochloric acid solutions:

Nature of solution.	Velocity of isomeric change in <i>N</i> /10-solutions (mols per litre per minute).	Thickness of layers of <i>N</i> /10- solutions of equal absorption capacity.
<i>N</i> -Hydrochloric acid	1.9×10^{-4}	18 mm.
Neutral.....	3.3×10^{-9}	24 mm.
Velocity ratio = 60,000.	Absorption-coefficient ratio = $24/18 = 1.3$.	

According to the view that the absorption capacity is determined by the rate of isomeric change, these two ratios should be equal or, at any rate, of the same order of magnitude, whereas experiment shows that the velocity ratio is about 50,000 times greater than the ratio of the absorption-coefficients. It may therefore be taken for granted that in the case of the simplest substances containing the $\cdot\text{CH}_2\cdot\text{CO}\cdot$ group, there is no relation whatever between the rate of isomeric change and the selective absorption of the ultra-violet light which is supposed to be characteristic of this grouping.

Summary.

It is shown in this paper (1) that the rate of isodynamic change of the ketones bears no relation to the rate at which these substances react with sodium hydrogen sulphite or hydroxylamine, and that the available data relating to these reactions are, moreover, not comparable.

(2) That the so-called persistence of selective absorption bands has no definite physical significance, and that comparable numbers for a group of similar substances can only be obtained by measuring the extinction-coefficients for the selectively absorbed radiation. Approximate values for the coefficients may be deduced from the extinction curves plotted from the absorption spectra at different dilutions.

(3) That there is no relation between the rates of isomeric change of the aliphatic ketones and the absorption-coefficients for the radiation of that frequency which is supposed to be characteristic of the $\cdot\text{CH}_2\cdot\text{CO}\cdot$ group.

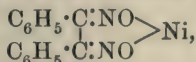
(4) That an alteration in the rate of isomeric change of acetone in the ratio of 60,000:1 has practically no influence on the absorption of the rays, the frequency of which corresponds with the "head" of the characteristic ultra-violet band.

CXLI.—*The Nickel Salts of the Benzildioximes.*

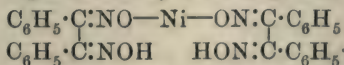
By FREDERICK WILLIAM ATACK.

THE formation of the nickel compounds of the 1:2-dioximes has been studied by Tschugaev (*Zeitsch. anorg. Chem.*, 1905, **46**, 144; *Ber.*, 1906, **39**, 3382; 1908, **41**, 1678; *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1466). He states that α -(*syn*-)dioximes form metallic compounds, and shows that in these only one of the two oximino-groups present has its hydrogen replaced by metal. He also repeatedly states that neither the β -(*anti*-) nor the γ -(*amphi*-)dioxime yields nickel salts. ("Die Fähigkeit zur Bildung der charakteristischen Dioxime kommt nur den *syn*-Modifikationen, nicht dagegen den *amphi*- und *anti*-Modifikationen der 1:2-Dioxime zu," *Ber.*, 1908, **41**, 1683).

Tschugaev's formula for the nickel compound of α -benzildioxime has been confirmed by the present author, and it has been found that this compound, like the original dioxime, does not form molecular compounds with solvents from which it crystallises. A nickel compound of γ -benzildioxime has been prepared, but no nickel compound of β -benzildioxime could be isolated. The nickel compound of γ -benzildioxime is obtained in the crystalline condition from chloroform solution or from benzene solution. One molecule of the compound crystallises with one of chloroform, and two molecules with one of benzene. Analysis and determination of the molecular weight, after freeing from chloroform or benzene, show the compound to have the composition $C_{14}H_{10}N_2O_2Ni$. Both of the oximino-groups in γ -benzildioxime would therefore appear to contain hydrogen atoms replaceable by metal, and the nickel compound is represented by the formula:



in which nickel enters into a ring. Tschugaev's assumption of a cyclic structure for the nickel compound of α -benzildioxime, based only on analogy to cobalt compounds which contain ammonia in addition to dioxime, would appear to be unnecessary. It would appear more probable that only one of the hydrogen atoms in α -benzildioxime is replaceable by metal, giving:



Tschugaev's failure to obtain the nickel salt of the γ -modification was probably due to the fact that his experiments were carried out in pyridine-alcohol solution, in which this salt is very soluble.

Attempts to prepare a nickel compound of β -benzildioxime have resulted only in the precipitation of nickel hydroxide.

The results obtained suggest that of the two oximino-groups present in 1:2-dioximes:

In the α -(*syn*-)modification, one group is basic, the other acidic;

In the β -(*anti*-)modification, both groups are basic;

And in the γ -(*amphi*-)modification, both groups are acidic.

These results suggest the possibility of extending the process to give a method for determining the configuration of oximes. In opposition to the statement of Tschugaev (*Zeitsch. anorg. Chem.*, 1905, **46**, 150), the chloro*amphi*-glyoxime of Hantzsch (*Ber.*, 1892, **25**, 709) has been found to give a yellow nickel salt, similar in properties to that from *amphi*-benzildioxime, whereas the chloro-*synglyoxime* gives a more stable red compound. Of the four camphorquinonedioximes, the α - and δ -modifications give yellow solutions with ammoniacal nickel solutions, the β -modification gives a red solution, and the γ -modification does not appear to give a nickel salt. These results are in agreement with the structures assigned to these dioximes by Forster in a recent paper (this vol., p. 662), and further agree with the results obtained by the same author (T., 1903, **83**, 514) for the reactions of these various modifications with ferrous sulphate and sodium hydroxide. The last-named results do not appear to have given any differentiation between the α -, β -, and δ -modifications, whereas ammoniacal nickel solutions give distinctive tests.

EXPERIMENTAL.

I. Behaviour of α -Benzildioxime.

α -Benzildioxime was prepared by the modified method of Auwers and V. Meyer (*Ber.*, 1888, **21**, 784) by digesting a methyl-alcoholic solution of benzil with an excess of hydroxylamine hydrochloride. The product was purified by washing with hot water, then with warm 50 per cent. alcohol, and was finally crystallised from boiling alcohol containing a trace of ammonia. The purified product was dried at 110°. It became brown at 231–232°, and melted and decomposed at 237°.

Alcohol and acetone solutions of the dioxime gave the bright red nickel salt with ammoniacal nickel solutions, which became yellowish-red on coagulation. The precipitation is quantitative in presence of an excess of nickel or of dioxime, and is therefore available for the detection and estimation of the oxime, as shown by the following experiment: A known weight of the oxime was dissolved in alcohol to which ammonia had been added, and a small

excess of an ammoniacal nickel sulphate solution over the amount required to precipitate the oxime was added. The precipitate was collected, washed with 50 per cent. alcohol, dried at 110°, and weighed:

α -Benzil-dioxime, gram.	Total nickel present, gram.	Nickel compound from α -dioxime, gram.	α -Dioxime found, per cent.	Excess nickel as α -dioxime compound, gram.	Total nickel found, gram.
0.2076	0.04538	0.2314	99.6	0.1832	0.04532
0.1422	0.01740	0.1588	99.8	trace	0.01736
0.1602	0.02748	0.1782	99.5	0.0718	0.02732

These results are calculated on the basis that the nickel salt has the composition $C_{28}H_{22}O_4N_4Ni$, which contains 10.93 per cent. of nickel. Thus this compound is composed of two molecules of dioxime, in which two atoms of hydrogen are replaced by metal.

This nickel compound is insoluble in alcohol, ether, or benzene. On recrystallising from chloroform, small, red, rectangular monoclinic crystals are obtained, which appear orange by transmitted light. The compound is not attacked by dilute acids, but is rapidly dissolved by potassium cyanide solution.

As in the case of the original dioxime, the nickel compound does not give any compounds which contain any of the solvent from which it has been crystallised.

II. Behaviour of β -Benzildioxime.

The sample of β -dioxime used was prepared by recrystallising a commercial sample from hot water, and drying at 110°, when the substance melted at 206—207°. The purified material was analysed by reduction with a known volume of standard titanous chloride solution, and estimation of the excess of reducing agent by means of standard methylene-blue solution. The results obtained showed that the dioxime was pure (99.9 to 100.2 per cent.).

On addition of an alcoholic solution of the β -dioxime to an ammoniacal solution of a nickel salt, a greenish-yellow precipitate separates, and can be identified as nickel hydroxide. If the alcoholic solution of the β -dioxime is too concentrated, a small amount of the dioxime is carried down on account of its lower solubility in the alcohol-water mixture. On using more dilute solutions, there is no carbon in the precipitate. For example: 0.2350 gram of the β -dioxime gave, with an ammoniacal solution containing 0.0550 gram of nickel, 0.0728 gram of precipitate dried at 105°. The solution remaining contained only traces of nickel on being tested by addition of an alcoholic solution of the α -dioxime. On solution of the precipitate in hydrochloric acid and precipitation with α -benzildioxime, the precipitate weighed 0.5020 gram, corre-

sponding with 0.0548 gram of nickel, which agrees with the weight of nickel in the solution used.

No nickel compound of β -benzildioxime has been isolated. On allowing a saturated aqueous solution of the β -dioxime to remain for several days in the presence of an ammoniacal nickel solution, after filtering from any precipitate which separates at first, the characteristic flocculent precipitate of the α -benzildioxime nickel salt was formed. The compound was identified by its insolubility in alcohol and reaction with a solution of potassium cyanide. In case an alcoholic solution of the β -dioxime is used, the product is mainly the nickel salt of γ -benzildioxime described below, mixed with a small amount of the nickel salt of α -benzildioxime. These experiments are of interest, as although the conversion of the α - and γ -dioximes into the β -dioxime is well known, there does not appear to have been any previous mention in the literature of the conversion of β -benzildioxime into the other modifications. Hantzsch has recorded, however (*Ber.*, 1892, **25**, 709), that dilute alkalis convert chloroantiglyoxime into the *amphi*-modification.

III. Behaviour of γ -Benzildioxime.

An alcoholic solution of γ -benzildioxime gives no apparent reaction with nickel sulphate solution until a small amount of ammonia has been added, when a buff-coloured precipitate is obtained. This precipitate is soluble in excess of ammonia, yielding a yellowish-brown solution, and in acids to a colourless solution. If ammonia is added cautiously, the yield is almost theoretical, one molecular proportion of the dioxime giving rise to one of the nickel salt. After drying in air, the product was a micro-crystalline powder, insoluble in water, but sparingly soluble in ether, methyl and ethyl alcohols, or light petroleum, and more soluble in acetone, chloroform, benzene, pyridine, or carbon tetrachloride. On recrystallising from chloroform and drying the crystals over sulphuric acid, the compound was found to contain one molecule of chloroform of crystallisation:

Nickel compound with chloroform of crystallisation, gram.	Loss in weight at 100°, gram.	Loss in weight, per cent.	Calculated for $C_{14}H_{10}O_2N_2Ni, CHCl_3$, per cent.
0.1076	0.0308	28.6	
0.1878	0.0546	29.1	28.7

Attempts to analyse the compound, freed from chloroform, by ignition failed, owing to the loss of nickel due to volatilisation. The product was finally analysed by conversion into nickel sulphate and estimation of the nickel by means of α -benzildioxime (compare *Analyst*, 1913, **38**, 316):

γ -Nickel compound, gram.	α -Nickel compound, gram.	Nickel in compound, per cent.	Calculated for $C_{14}H_{10}O_2N_2Ni$, per cent.
0.0768	0.1370	19.54	
0.1332	0.2396	19.66	19.78
0.0838	0.1490	19.44	

The percentage of nitrogen in the compound was determined by the Kjeldahl method:

Found, $N = 9.56$. $C_{14}H_{10}O_2N_2Ni$ requires $N = 9.44$ per cent.

The compound is decomposed by concentrated hydrochloric acid, with the ultimate formation of the β -dioxime. Glacial acetic acid converts the substance superficially into the nickel salt of the α -dioxime, which is also formed on boiling with dilute hydrochloric or acetic acid. Very dilute acetic acid dissolves the compound, part being reprecipitated unchanged on careful addition of ammonia. Solutions of alkalis and potassium cyanide have no action on the compound. Addition of a solution of the α -dioxime to the γ -nickel compound gives a partial conversion to the α -nickel compound. On heating to 180° , the nickel salt of the α -dioxime is not affected, whereas that of the γ -dioxime decomposes, yielding as one of the products the nickel salt of the α -dioxime.

The molecular weight of the compound as determined by the ebullioscopic method was found to be normal in benzene solution:

0.1618 gram in 18.0 grams of benzene gave $E = 0.088^\circ$. $M.W. = 276$.

$C_{14}H_{10}O_2N_2Ni$ requires $M.W. = 297$.

Other salts of γ -dioximes have been prepared, and are being investigated, including the deep brown cobalt compound of γ -benzildioxime. Further investigations of these metallic salts and of the interconversion of the dioximes are in progress, with a view to establish whether the reactions described above are due to the interspatial arrangements of the oximino-groups or to other causes.

In conclusion, the author desires to thank Prof. Knecht for having afforded him facilities for carrying out these investigations.

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CXLII.—*The Rotatory Dispersive Power of Organic Compounds. Part III. The Measurement of Magnetic Rotatory Dispersion.*

By THOMAS MARTIN LOWRY.

IN the very earliest stages of these investigations it became apparent that great importance would attach to comparative measurements of optical and magnetic rotatory power over a wide range of the spectrum, since without this twofold examination it would be impossible to specify completely the optical properties of the substances selected for investigation. After consultation with the late Sir William Perkin, I received his generous permission to develop this branch of a field of work which he had made peculiarly his own.

The Magnet.—The magnet (Fig. 1) constructed for this purpose was a modification of the one designed for Sir William Perkin (T., 1906, **89**, 610) by Prof. Mather. Perkin's magnet was energised by a large battery of primary cells. In order to use the limited power of the battery to the best advantage, the magnet was wound with massive copper wire, 3.05×2.7 mm. in section, of which 2000 turns were used, the weight of copper being about 110 kilos. The wire was arranged in two concentric coils, each having a resistance of about 8 ohms. These were used in parallel with a total current of 12.5 amp. under a pressure of 50 volts. When placed in the centre of the magnet, a column of water 100 mm. in length produced a rotation of 6° in the position of the plane of polarisation on reversing the current. The corresponding rotation for a column of 175 mm. was $9^\circ 3'$, sodium light being used in each case.

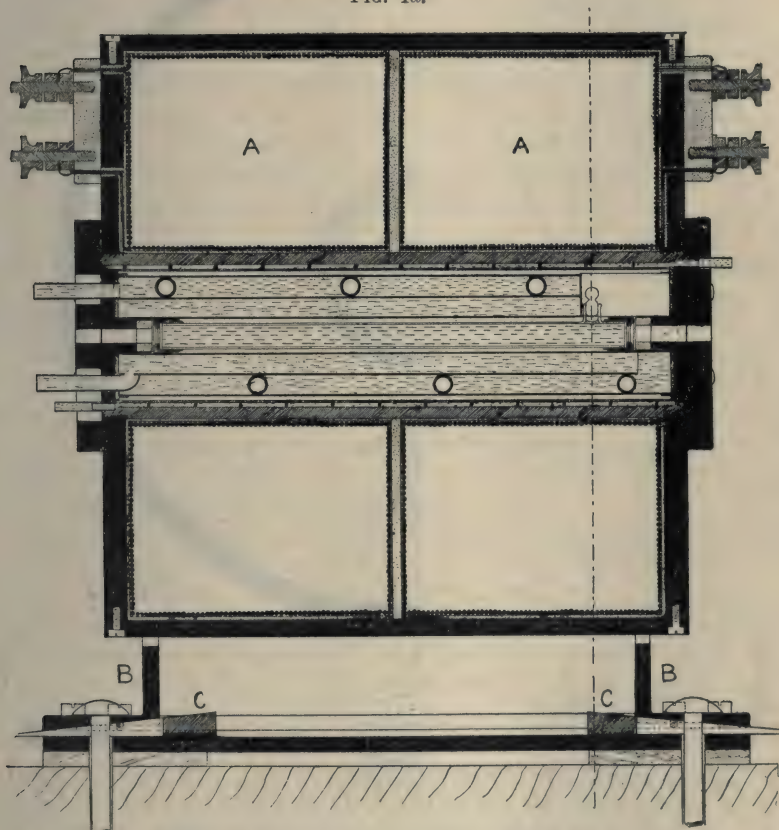
In adapting this design, I had the great advantage of receiving instruction and advice from Prof. Mather. The intention was to construct a magnet which could be operated directly from the street mains under a pressure of 200 volts. Under these conditions it was not necessary to exercise so strict an economy in the use of power, the chief restriction being imposed by the risk of overheating the magnet. It was therefore possible to use smaller wire, and so to reduce greatly the total weight of copper and the size and cost of the magnet.

The Coils.—The magnet (Fig. 1) contained two coils, AA, each coil being composed of 3810 turns of No. 18 copper wire. The coils were wound side by side on a brass tube, and were brought out to separate terminals. They were designed to be used in series

on a 200 volt circuit, or in parallel on a 100 volt circuit. The resistance of each coil was about 25 ohms. The coils were separated from one another by an ebonite disk, and were insulated from the casing by means of "presspahn"; the terminals were mounted on ebonite blocks, and the leads brought out through grooves bushed with ebonite.

Armatures.—In order to lead the lines of force to the axis of

FIG. 1a.



Section of electromagnet. (About $\frac{1}{10}$ th full size.)

the magnet, the coils were enclosed in an iron case, made by screwing an iron disk on to each end of the brass tube on which the coils were wound, and then sliding a length of iron pipe over the whole; twelve screws were used at each end to fix the iron pipe to the two iron disks.

In Perkin's magnet no further provision was made for bringing

the lines of force to the axis; there was therefore very considerable divergence as the lines of force passed from the centre towards the ends of the magnet; the strength of the field also decreased, at first

FIG. 1b.

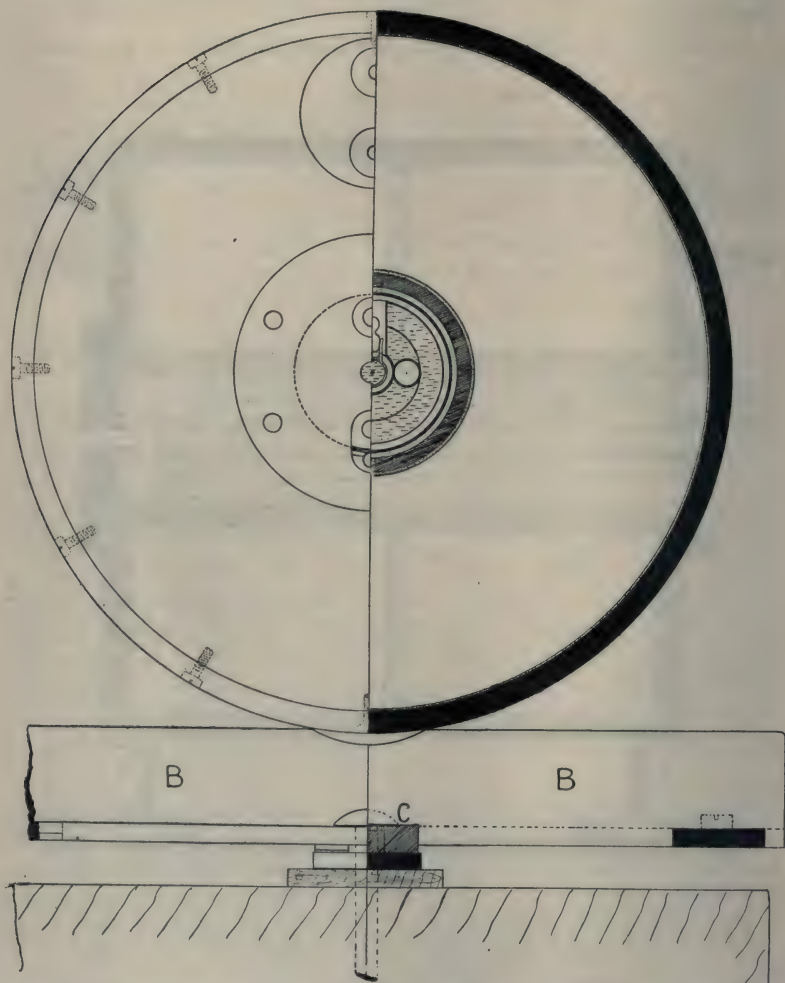


Diagram of electromagnet. (Half-elevation and half-section, about $\frac{3}{10}$ th full size.

slowly, and then rapidly, until at the ends it had diminished to a quarter of its value at the centre. In the design shown in Fig. 1 this defect was very largely remedied by the addition of four semicircular iron plates, which closed up the ends of the hollow

bobbin, but could be removed in order to lift the test-substances in and out; these iron plates were pierced at the centre in order to allow a beam of polarised light to pass along the axis; provision was also made for the various water tubes to pass through the plates. The addition of these end-plates had the effect of increasing the strength of the field and rendering it almost uniform from end to end. The lines of force were still, however, slightly divergent, and there was still some diminution in the strength of the field towards the ends of the magnet. Further provision was therefore made for leading in the lines of force by means of iron armatures pierced in the centre, and extending right up to the ends of the tube containing the liquid under examination. These armatures caused the lines of force to converge towards them, but by filing them down and replacing the metal by pieces of pierced cork a point was reached at which the convergence disappeared, and there was no marked difference in the strength of the field at the centre and at the ends of the tube. The magnetic circuit, including the iron case, the end-plates, and the armatures, is shown in solid black in the sectional drawings of the magnet, and can easily be traced without the aid of any lettering.

The addition of the end-plates and the armatures increased the readings of magnetic rotatory power by only about 5 per cent., as most of the improvement took place in the spaces beyond the ends of the tube containing the liquid under examination. But it was considered to be a distinct advantage to have secured straight lines of force and a uniform field throughout.

A much greater advance was made in the examination of shorter columns of liquid. The column shown in Fig. 1 was 200 mm. in length, but in many cases the material available was only sufficient to fill a shorter tube. If the short tube had been placed in the same jacket, the readings would have been diminished in the same proportion as the length. Attempts were made to remedy this defect by carrying one of the armatures right down the centre of the water-jacket until it touched the shorter tube; but the quantity of iron in the extended armature was not sufficient to carry so heavy a magnetic field, and no marked increase was produced in the readings. Great success, however, attended the use of the heavy iron armatures shown in Fig. 1 of Part I of this series of papers (this vol., p. 1066). When these were used with a shortened water-jacket and a 100 mm. tube, the readings were only 5 per cent. less than with a tube 200 mm. in length; it was therefore a matter of indifference whether the readings were taken with the longer or the shorter column of liquid.

Water-jackets.—Attention may also be directed to the water-

jackets used in connexion with the magnet. The interior of the magnet was lined with a thin layer of water, drawn from the mains, and compelled to circulate round the lining by a spiral wire baffle. This water-lining had a most important influence in cooling the magnet, and had the further advantage of protecting the isothermal flow in the main water-jacket from the heating effects of the current.

The maintenance of a constant temperature was provided for by placing the test-liquid inside a double-walled water-jacket operated in connexion with a thermostat (*Trans. Faraday Soc.*, 1907, **3**, 119). A flow of about 1 litre per minute was maintained from the thermostat through the jacket and back to the bath, but it was essential that the return flow should not be heated by the current in the magnet, otherwise the cooling of the magnet would be effected mainly at the expense of the bath; the water lining was therefore an essential factor when making measurements at a definite regulated temperature. The double-jacketing of the main water-jacket was convenient in bringing the entrance and exit tubes to the same end of the magnet, but was also an important help in securing an accurate control of temperature. The total change of temperature in the circuit did not often exceed 0.1° , and practically the whole of this would take place on the outer surface of the jacket, the change in the inner jacket being quite inappreciable.

Supports.—The magnet was supported on a pair of angle-iron rails (*BB*, Fig. 1). These could be raised and lowered by means of brass wedges, *CC*, which were slotted in order to allow the rails to be bolted through to the timber mounting of the apparatus. The wedges were placed in a central position immediately under the magnet, so that there should be no tendency to twist the timber supports. An independent support was provided at the end of the longer arm of the rails (not shown), so that the magnet could be rolled out of the way without introducing any new strain into the system.

The Electric Current.—In Perkin's experiments the whole of the current passing through both coils of the magnet was sent through a galvanometer, the current from the battery being regulated to give a constant deflexion. The magnet now described was arranged in series with a potentiometer, so that the current could be measured or controlled by a zero-method instead of by a deflexion-method. The current from the magnet passed through a coil of manganin wire, *D*, Fig. 2; two contacts were provided, leading from this wire through a double key, *KK*, to a standard cadmium cell, *C*, and a sensitive Ayrton-Mather galvanometer, *G*; the positions of the contacts were adjusted so that no deflexion took place when

the current through the magnet was about $2\frac{1}{2}$ amperes. When this current was used, readings could be taken almost continuously, the cooling effect of the water-lining being almost sufficient to balance the heating effect of the current when the magnet was getting to its highest temperature.

The current passing through the magnet was regulated by means of (1) a carbon resistance *E*, (2) a sliding resistance of 2 ohms *F*, (3) a series of manganin coils *H* of resistance, $1 + 1 + 2 + 4 + 4 + 8 = 20$ ohms, which could be short-circuited to compensate for the increasing resistance of the magnet.

The current was regulated by hand to compensate for the varying pressure on the mains; occasionally a sudden "kick" of the galvanometer would necessitate the rejection of a reading, but as a rule the uncontrolled fluctuations of current were too small to cause any marked effect, especially when a series of readings was being taken. Only when carbon disulphide (giving a deflexion of $\pm 20^\circ$) was being read was it possible to see in the polarimeter the variations of rotation produced by fluctuations of current-strength. Actual measurements showed that a deflexion of 40 inches on the galvanometer scale corresponded with an alteration of 1 per cent. in the readings, so that a deflexion of 4 inches would introduce an error of only 0.1 per cent. on the plus or minus reading, or 0.05 per cent. on the double rotation produced by reversing the current; little difficulty was experienced in regulating the current within these limits during the greater part of the time when observations were being made, and it was only necessary to reserve the right to reject an occasional discordant reading in order to remove all trouble from this source. The potentiometer method is certainly much more sensitive than any method in which the whole current is passed through a galvanometer, either with or without a shunt, and it has the great advantage that small fluctuations of current are very readily seen.

The arrangement of the electrical circuits is shown in Fig. 2, where:

A is a wall-plug, connected to the mains in such a way that the magnet was joined up with the *negative* high-tension lead.

B is a reversing switch controlling the direction of the current in the magnet.

G is a galvanometer in series with a cadmium cell *C* and a double key *KK*, this circuit being arranged in parallel with the manganin coil *D*, which carries the main current of the magnet.

E is a carbon-plate rheostat.

F is a sliding wire resistance.

HH are sets of manganin resistances with short-circuiting switches.

Tests.—The following tests were made:

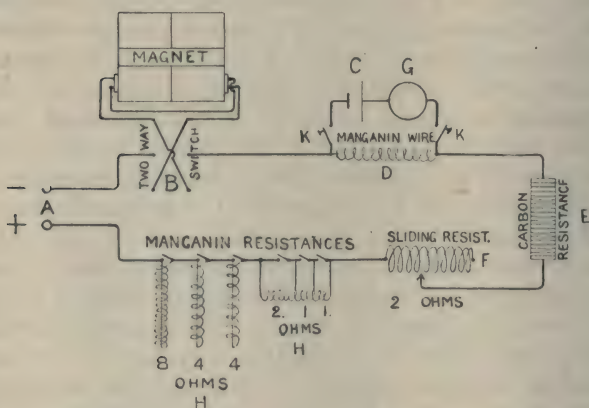
(a) *Resistance.*—The resistances of the two coils were measured, and found to be 25.17 and 25.86 ohms respectively.

(b) *Insulation.*—The insulation-resistance between the two coils was found to be 372 megohms; the resistance between the coils and the iron casing was found to be 333 megohms. These measurements refer to the coils after the magnet had been reopened and baked dry, as described in the following paragraph.

(c) *Temperature-coefficient.*—As the magnet was used over a considerable range of temperatures, it was important to know whether this had any influence on the readings. In the earliest stages of the work a distinct effect was found, using carbon

FIG. 2.

DIAGRAM OF ELECTRICAL CONNEXIONS



disulphide as a sensitive test-substance, giving a double-deflexion of over 40° . In five experiments the readings decreased by 0.14° , 0.16° , 0.16° , 0.14° , and 0.16° when the magnet was hot. This effect was traced to defective insulation; in constructing the water-lining the screw-thread on the ends of the brass tube carrying the coils had been cut into, and water escaped into the coils; the first drying-out of the coils was evidently not successful, but after opening and rebaking the magnet the defect was remedied. A test for temperature-coefficient then gave the following figures:

Magnet cold	$\alpha = 41.42^\circ$	41.40°	41.47°	Mean 41.43°
Magnet hot	$\alpha = 41.43^\circ$	41.43°		

(d) *Residual Magnetism.*—As the casing of the magnet was constructed of mild steel and not of wrought iron, it was important

to know whether a permanent magnetic field remained after switching off the exciting current. This point was tested by reading the polarimeter, with a tube of carbon disulphide in the magnet, after the current had been switched on and off, first in one direction and then in the other. The first test gave readings which were absolutely identical. A second test gave the following figures:

Magnet on (right).....	201·55°	magnet off	222·28°
„ (left)	242 98°	„	222·27°
Double deflexion	41·43°	Residue	-0·01°

The readings agree within 0·01°, and this difference is in the opposite direction to that which would be produced by residual magnetism.

(e) *Strength of Field*.—The substantial uniformity of the field in the region containing the liquids under examination was shown by actual measurements of the strength of the field, carried out with the help of a small solenoid and a ballistic galvanometer. Readings at intervals of 3 cm. gave the following figures:

Current.....	1·7 amps. ...	851	869	872	862	868	854 Gauss.
	1·95 „ ...	1013	1024	1041	1030	1038	1038 „

For a current of 1 ampere the average strength of the field was:

First series	510	} Mean 520 Gauss.
Second „	530	

Polarimeter Tubes.—The liquids for examination were enclosed in glass tubes surrounded by the double water-jacket already referred to. The aperture of this jacket was 15 mm., and the first tubes were constructed to occupy the whole of the available width; a side-tube, with stopper, for filling the tube, projected into a slot at one end of the water-jacket. Later, on account of the scarcity of some of the liquids and the serious risk of loss through the loosening of cemented disks, narrower tubes were used of about 8 mm. internal diameter; space was then available for brass screw-caps to reinforce the cement in holding the disks in place, as shown in Fig. 1. As equalisation of temperature across the air-gap was slow, the tubes were usually filled and put in place on the preceding evening, but they were then so completely enclosed by the brass caps, corks, and iron armatures that the adjustment of temperature was probably perfect.

The lengths of the polarimeter tubes were measured, and were found to differ in some cases by about 0·2 mm. from the nominal length of 200 mm.; this error is insignificant, as it would only affect the readings by 0·01°, and could easily be allowed for. A slightly larger error was detected when a comparison was made with different water-jackets containing tubes of equal length.

Disks.—In order to facilitate the extension of the work to the ultra-violet region, silica glass was selected as the material for the disks at the ends of the polarimeter tubes. This material has the further advantage of constant composition, so that additional disks of identical magnetic rotatory power could be ordered at any time. The choice was, in many respects, however, not a fortunate one, as it is very difficult to secure silica plates which will appear homogeneous when examined with monochromatic polarised light, and even these require to be set up carefully if they are to be entirely free from all traces of optical rotatory power. For a research confined to the visible region of the spectrum a series of disks cut from a single glass plate would certainly prove less troublesome.

In measuring the magnetic rotatory dispersion of liquids, it is necessary to know the rotation produced by the disks when using light of each different wave-length. As it was difficult to secure trustworthy readings of these very small rotations, the rotatory dispersive power of the silica was determined once for all by building up a column of 24 mm. in the centre of the magnet. The readings were:

Li	6708	1·19°	Ratio to green	0·63
Hg	5461	1·89		
Hg	4359	3·17	Ratio to green	1·67

The values for other wave-lengths could then be deduced by comparison with longer columns of another substance of equal dispersive power; for the earlier observations, in which a column of water 200 mm. in length gave a rotation of 12·60° for light of wave-length 5461, the corrections for disks 2 mm. in thickness were:

Li 0·20	Cd 0·21	Na 0·25	Hg 0·27	Hg 0·30	Cd 0·35	Cd 0·40	Cd 0·43	Hg 0·50°
Red.		Yellow.		Green.		Blue.		Violet.

In the later readings, with a smaller current, but with the iron armatures inserted, the water-value was 11·96°; the corrections for disks 1 mm. in thickness were then:

Li 0·10	Na 0·15	Hg 0·16	Hg 0·27
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on a 200 mm. tube. For a column of 100 mm. of water, the water-value was 11·32°, and the disk corrections were:

Li 0·30	Na 0·40	Hg 0·45	Hg 0·75
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The absolute values of the disk corrections were determined by reading an empty tube with a double thickness of disks and green mercury light.

The Readings.—In reading magnetic rotations, series of ten readings were taken with the current in the magnet flowing in opposite directions in alternate series. The number of series taken

for each wave-length ranged from about 6 to 12, giving the same number of difference-readings between alternate series. In nearly every case this process was repeated *de novo*, and, if necessary, a third group of 6 to 12 series was taken in order to secure a trustworthy average. Each figure tabulated for the magnetic rotatory power of a substance is therefore the result of some 100 to 200 (or more) independent settings of the instrument. Under these conditions casual variations of current strength were of no importance.

The aim in every case was to secure results which could be relied on to one unit in the third decimal of the dispersion-ratios, or, roughly, 1 part per 1000, corresponding with an accuracy of about 0.01° in the individual rotations.

The experiments on magnetic rotatory dispersion were carried out with the help of grants from the Government Grant Fund of the Royal Society. The erection of the apparatus, including the whole of the wiring, was carried out by Mr. W. P. Paddison, who also made many of the earlier measurements. The later measurements were made with the help of Mr. H. R. Courtman. In each case the author desires to acknowledge his indebtedness and to express his thanks.

CXLIII.—*Some Derivatives of Desylamine.*

By ALEX. MCKENZIE and FRED BARROW.

FOR some time back the authors have been engaged in the examination of certain desylamine derivatives in connexion with an investigation, which is at present in progress, on the optically active modifications of the base.

Desylamine hydrochloride was prepared by Gabriel and Neumann (*Ber.*, 1890, **23**, 995) from desylphthalamic acid, but the isolation of the salt was accomplished with some difficulty. The free base was characterised by means of its platinichloride and picrate. Braun's attempts to isolate the base (*Ber.*, 1889, **22**, 557) met with no success, owing to its instability. On the other hand, Pschorr and Brüggemann (*Ber.*, 1902, **35**, 2740) were successful in obtaining the pure base from the hydrochloride, which they prepared by modifying Braun's method of reducing benzilmonoxime by stannous chloride.

The classical researches of Gabriel on amino-ketones have shown that these compounds can be prepared by the application of the Friedel-Crafts' method to the phthalyl derivatives of amino-acid

chlorides. Utilising this method, we converted phenylaminoacetic acid into desylamine hydrochloride. Pfaehler (*Ber.*, 1913, **46**, 1700) has just described the preparation of desylphthalimide by Gabriel's method, and we have therefore decided to publish our experiments on the same subject at the present time.

Phenylaminoacetic acid was converted into its phthalyl derivative, $C_8H_4O_2 \cdot N \cdot CHPh \cdot CO_2H$, by heating with phthalic anhydride at $160-170^\circ$; carbon dioxide was eliminated at 300° , and benzylphthalimide was produced. α -Phthalyliminophenylacetic acid was then converted by means of thionyl chloride into its acid chloride, from which desylphthalimide was formed by the action of benzene and aluminium chloride.

Desylphthalimide was also prepared by the interaction of desyl chloride and potassium phthalimide. When the latter action was conducted in the presence of nitrobenzene at $150-160^\circ$, dibenzoylstilbene was formed as a by-product.

Desylphthalimide was converted into desylphthalamic acid, $C_8H_4O_2 \cdot N \cdot CHPh \cdot COPh \rightarrow CO_2H \cdot C_6H_4 \cdot CO \cdot NH \cdot CHPh \cdot COPh$, from which desylamine hydrochloride was prepared by hydrolysis (compare Gabriel and Neumann, *loc. cit.*).

We also take the opportunity of describing in the present paper the preparation of 2:4:5-triphenyloxazole by the dehydration of benzodesylamide. The action of magnesium methyl iodide, magnesium α -naphthyl bromide, and magnesium phenyl bromide on desylamine hydrochloride gave satisfactory yields of the corresponding amino-alcohols.

It may be stated that we have already resolved α -phthalyliminophenylacetic acid into its optically active components, from which we hope to obtain the active desylamines. The preparation of the latter compounds from other sources is also being studied.

EXPERIMENTAL.

Formation of Desylamine Hydrochloride from Phenylaminoacetic Acid.

α -Phthalyliminophenylacetic acid, $C_8H_4O_2 \cdot N \cdot CHPh \cdot CO_2H$, was prepared by heating phenylaminoacetic acid with phthalic anhydride for two hours at $160-170^\circ$ (compare Ulrich, *Ber.*, 1904, **37**, 1689). It melted at $170.5-171.5^\circ$, whereas Ulrich gives 168° (Found, $C=68.5$; $H=4.0$. Calc., $C=68.3$; $H=3.9$ per cent.).

When phenylaminoacetic acid was heated for one hour at about 300° with slightly more than the calculated quantity of phthalic anhydride, a brown oil was formed, and this was dissolved in ethyl alcohol. The substance which separated was purified by crys-

tallisation from ethyl alcohol. It formed brittle, yellow prisms, melted at $116\text{--}117^\circ$, and was obviously benzylphthalimide (Found, $C=75.6$; $H=4.8$. Calc., $C=75.9$; $H=4.7$ per cent.). The same compound was also produced by the elimination of carbon dioxide by heating α -phthalyliminophenylacetic acid at $320\text{--}350^\circ$ for thirty minutes.

Four grams of the phthalyl acid were heated for half an hour on the water-bath with 8 grams of thionyl chloride, the excess of which was then removed. On the addition of 40 c.c. of benzene to the resulting viscid, fluorescent oil, the acid chloride* began to crystallise. Four grams of aluminium chloride were added, and the mixture boiled for half an hour, and then poured into dilute sulphuric acid. The resulting product was separated from the benzene and purified by crystallisation, first from ethyl alcohol, and finally from glacial acetic acid. Yield 2 grams. It was identified as desylphthalimide, $C_8H_4O_2 \cdot N \cdot CHPh \cdot CPh$, by its melting point and analysis (Found, $C=77.1$; $H=4.5$. Calc., $C=77.4$; $H=4.4$ per cent.).

Desylphthalimide was also prepared by the interaction of desyl chloride and potassium phthalimide. Desyl chloride (15.5 grams), prepared by the action of thionyl chloride on benzoin, was heated on the water-bath for two hours with potassium phthalimide (11.5 grams). The pasty product was boiled with glacial acetic acid, and water was added to the filtrate until turbidity was produced. The solid which separated was crystallised from a mixture of ethyl alcohol and pyridine; 5.5 grams of desylphthalimide, melting at $155\text{--}156^\circ$, were obtained.

When the latter action was conducted under the following conditions, dibenzoylstilbene was formed as a by-product. A mixture of desyl chloride (21 grams) and potassium phthalimide (17 grams) was heated with 20 c.c. of nitrobenzene for one and a-half hours at $150\text{--}160^\circ$. Water was then added, and the nitrobenzene removed by steam distillation. The resulting solid was crystallised from glacial acetic acid, and the product (19 grams) was a mixture of desylphthalimide and dibenzoylstilbene. Six grams of this mixture were crystallised three times from a mixture of ethyl alcohol and pyridine, when the pure desylphthalimide, melting at $155\text{--}156^\circ$, was obtained. The solid (4.2 grams), obtained by treating the mother liquors with water, was warmed for ten minutes with 50 c.c. of aqueous potassium hydroxide (1.8*N*). The residue (2.2 grams) was purified by crystallisation from a mixture of pyridine and alcohol, when dibenzoylstilbene separated as a felted

* This compound has been isolated by Pfæhler (*Ber.*, 1913, 46, 1705), who prepared it by the action of phosphorus pentachloride on the acid.

mass of colourless, slender needles, which melted at 207—208°,* and gave the characteristic colour reaction of this compound with concentrated sulphuric acid (Found, C=86·4; H=5·4. Calc., C=86·6; H=5·2 per cent.).

From the above-mentioned mixture of desylphthalimide and dibenzoylstilbene, desylamine hydrochloride was isolated in the following manner. 12·3 Grams were heated on the water-bath for half an hour with 50 c.c. of aqueous sodium hydroxide (1·008*N*). The insoluble dibenzoylstilbene (1·1 grams) was removed, and the filtrate acidified with hydrochloric acid. Desylphthalamic acid, melting at 166—167°, was precipitated, water was added, and a current of hydrogen chloride passed until saturation occurred. After boiling for one and a-quarter hours, and then cooling, phthalic acid separated, and from the filtrate, by concentration, crystals of desylamine hydrochloride and phthalic acid were obtained. The free base was liberated by alkali and extracted with ether; a current of hydrogen chloride was passed through the ethereal solution, when 6 grams of desylamine hydrochloride, in an amorphous condition, were precipitated. The salt was obtained in colourless needles, melting and decomposing at 233—234° by solution in water and addition of concentrated hydrochloric acid.

The method of Pschorr and Brüggemann (*loc. cit.*) is very convenient for the preparation of desylamine hydrochloride on the large scale; thus, in one preparation, we obtained 75 grams from 105 grams of benzilmonoxime.

Conversion of Desylamine Hydrochloride into 2:4:5-Triphenyl-oxazole.

Robinson (T., 1909, **95**, 2167; compare also Lister and Robinson, T., 1912, **101**, 1297) has described a method of synthesising oxazoles depending on the dehydration of acylated amino-ketones by sulphuric acid.

Desylamine hydrochloride was accordingly benzoylated by the Schotten-Baumann method. *Benzodesylamide*, $\text{NHBz}\cdot\text{CHPh}\cdot\text{COPh}$, crystallises from dilute alcohol in rosettes of slender, colourless needles, and melts at 139—140°:

0·1937 gave 0·5663 CO_2 and 0·0968 H_2O . C=79·7; H=5·6.

$\text{C}_{21}\text{H}_{17}\text{O}_2\text{N}$ requires C=80·0; H=5·4 per cent.

Benzodesylamide (1·5 grams) was warmed with concentrated sulphuric acid (5 c.c.) for about two minutes, and the product

* Japp and Klingemann (T., 1890, **57**, 688) state that they were unable to raise the melting point of dibenzoylstilbene ("acicular oxylepiden") above 210—211°, whereas Zinin gives 220° as the melting point.

added to water. The solid which separated was crystallised from ethyl alcohol. 1.2 Grams of colourless needles, melting at $115.5-116.5^\circ$, were obtained. The compound was obviously

2:4:5-triphenyloxazole, $\text{C} \cdot \text{Ph} : \text{CPh} \begin{matrix} \diagup \\ \text{N} = \text{CPh} \end{matrix} > \text{O}$, and is identical with

Laurent's "benzilam," for which the correct constitution was first suggested by Japp (T., 1883, **43**, 11), who gives the melting point as 115° (Found, C=84.3; H=5.2; N=4.7. Calc., C=84.8; H=5.1; N=4.7 per cent.).

The substance dissolves easily in benzene, the solution exhibiting a feeble, blue fluorescence.

β -Hydroxy- $\alpha\beta$ -diphenylpropylamine.

Desylamine hydrochloride (5 grams) was gradually added within five minutes to the Grignard reagent prepared from 17 grams of methyl iodide. The action was vigorous, and the solid dissolved. After one hour, the liquid was boiled for thirty minutes. The additive compound was decomposed by ice and ammonium chloride, and 4 grams of a yellow crystalline solid were obtained after removal of the ether. The compound was obtained pure, by crystallisation first from dilute alcohol, and finally from petroleum (b. p. $60-80^\circ$). Yield, 2 grams.

β -Hydroxy- $\alpha\beta$ -diphenylpropylamine, $\text{NH}_2 \cdot \text{CHPh} \cdot \text{CMePh} \cdot \text{OH}$, separates from petroleum in glassy, colourless needles, grouped in rosettes, and melts at $108.5-109^\circ$. It dissolves readily in cold ethyl alcohol, acetone, or benzene, and is insoluble in water:

0.2143 gave 0.6194 CO_2 and 0.1487 H_2O . C=78.8; H=7.8.

$\text{C}_{15}\text{H}_{17}\text{ON}$ requires C=79.2; H=7.5 per cent.

In the change $\text{NH}_2 \cdot \text{CHPh} \cdot \text{COPh} \rightarrow \text{NH}_2 \cdot \text{CHPh} \cdot \text{CMePh} \cdot \text{OH}$, a second carbon atom in desylamine becomes asymmetric, and a mixture of unequal amounts of two isomeric amino-alcohols might on theoretical grounds be expected. Only one amino-alcohol was, however, isolated.

β -Hydroxy- $\alpha\beta$ -diphenyl- β -naphthylethylamine.

This compound was prepared from desylamine hydrochloride (5 grams), and the Grignard reagent obtained from 25 grams of α -bromonaphthalene. The additive compound was decomposed by ice and ammonium chloride, and on this occasion the amino-alcohol was obviously very sparingly soluble in ether. It was collected and crystallised from ethyl alcohol. Yield, 3 grams.

β -Hydroxy- $\alpha\beta$ -diphenyl- β -naphthylethylamine,

$\text{NH}_2 \cdot \text{CHPh} \cdot \text{CPh}(\text{C}_{10}\text{H}_7) \cdot \text{OH}$,

is sparingly soluble in ethyl alcohol, from which it separates in iridescent plates. It melts at 191—192°, and gives an emerald-green coloration when dissolved in cold concentrated sulphuric acid:

0.2462 gave 0.7662 CO₂ and 0.1378 H₂O. C=84.9; H=6.3.

C₂₄H₂₁ON requires C=84.9; H=6.3 per cent.

It forms a hydrochloride, which melts and decomposes at about 215°.

It was converted by means of nitrous acid into diphenyl- α -naphthyl glycol, prepared by Acree from benzoin and magnesium α -naphthyl bromide (*Ber.*, 1904, **37**, 2764).

β -Hydroxy- $\alpha\beta$ -triphenylethylamine.

Desylamine hydrochloride (5 grams) was acted on by the Grignard reagent prepared from 19 grams of bromobenzene. The crude product was purified by crystallisation from ethyl alcohol. Yield, 3 grams.

β -Hydroxy- $\alpha\beta$ -triphenylethylamine, NH₂·CHPh·CPh₂·OH, separates as a white, crystalline powder, and melts at 154.5—155°:

0.2082 gave 0.6308 CO₂ and 0.1272 H₂O. C=82.6; H=6.8.

C₂₀H₁₉ON requires C=83.0; H=6.6 per cent.

It forms a hydrochloride, which is sparingly soluble in water.

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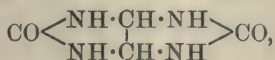
CXLIV.—*The Constitution of Allantoin.*

By ARTHUR WALSH TITHERLEY.

GRIMAUX'S formula for allantoin (I), whilst consistent with its synthesis by various methods and with many of its properties, fails to express the peculiar symmetry which its molecule possesses. This symmetry is discerned, for example, in the production of the same β -methylallantoin by oxidation of both 1- and 7-methyluric acid, and of the same α -methylallantoin from the three isomeric forms (α -, δ -, and ζ -) of 3-methyluric acid and from 9-methyluric acid (Fischer and Ach, *Ber.*, 1899, **32**, 2723; Hill, *Ber.*, 1876, **9**, 1090). Behrend (*Annalen*, 1904, **333**, 144) has explained these relations by assuming that molecular rearrangement occurs during the oxidation. Mendel and Dakin (*J. Biol. Chem.*, 1910, **7**, 153) explain the optical inactivity of allantoin, which in Grimaux's

formula possesses an asymmetric carbon atom by racemisation due to tautomerism.

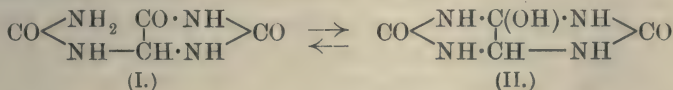
Biltz and Behrens (*Ber.*, 1910, **43**, 1996) adduce chemical evidence for the presence of the grouping $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot$ in allantoin as also does Fenton (*T.*, 1903, **83**, 187; Fenton and Wilks, *Proc. Camb. Phil. Soc.*, 1911, **16**, 64), but Biltz (*Ber.*, 1910, **43**, 2000) shows that as allantoin may be quantitatively reduced to "acetylene di-urein" (glycoluril):



the symmetrical formula (II) is conceivable.

Although such a symmetrical formula would at once explain the relation of the two methylallantoins to the methyluric acids, Biltz, on the whole, prefers Grimaux's unsymmetrical formula in view of the decomposition of allantoin by sodium hypochlorite (Biltz and Behrens, *loc. cit.*).

The author suggests that the apparently contradictory facts relating to allantoin can best be reconciled by the simple assumption of tautomerism involving the monocyclic unsymmetrical Grimaux formula on the one hand, and dicyclic formula rejected by Biltz on the other, thus:



Such tautomerism is analogous to the so-called "metoxazone tautomerism" observed by the author among the *O*-acyl and *N*-acyl derivatives of salicylamide (*T.*, 1906, **89**, 1318; 1907, **91**, 1419; 1909, **95**, 908; 1910, **97**, 200), and it is occasioned in all these cases by the wandering of an amidic or hydroxylic hydrogen atom to an oxygen or nitrogen atom in such a way as to produce either a closed or open chain system.

The tautomerism postulated by Mendel and Dakin is improbable, since it is of the keto-enolic type, which requires for its manifestation the influence of negative groups such as are absent in the allantoin molecule. Such keto-enolic tautomerism should, in fact, appear, with consequent rapid racemisation, in α -amino-acids and similarly constituted compounds where it is not apparent, if Mendel and Dakin's theory were to be accepted.

Although on other grounds it appears necessary to assume with Behrend (*loc. cit.* and *Annalen*, 1909, **365**, 21) that in the oxidation of uric acid an intermediate symmetrical compound is formed, it is not necessary to assume that allantoin is derived from this compound, and the relation of the two methylallantoins to the

four structurally isomeric methyluric acids is at once intelligible if it is granted that allantoin in its tautomeric form is a symmetrical compound.

It is probable that, as with other tautomeric substances, solutions of allantoin contain both forms in equilibrium, which is disturbed by chemical agencies. In its metallic salts and in solution in alkalis it is doubtless correctly represented by the unsymmetrical formula, which, on account of the secondary amide grouping, $\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot$, present, would function as a weak acid. In solution in mineral acids, on the other hand, where allantoin forms unstable salts readily dissociated by water, it is possible that the more basic symmetrical formula is the correct one. Evidence of tautomeric change during salt formation is to be found in the fact, observed by the author, that allantoin dissolves in nitric acid (D 1.4) to a clear solution, which, after a few minutes, deposits practically quantitatively the crystalline nitrate first isolated by Mulder (*Annalen*, 1871, **159**, 352). This nitrate, which melts at 154° , is very similar in properties to carbamide nitrate, and it is probably the open-chain salt. Carbamide does not pass into solution in nitric acid in this way before separating out as nitrate, and the different behaviour of allantoin would be intelligible on the supposition that a soluble nitrate of the dicyclic base is first formed. The latter would come into equilibrium with the open-chain nitrate, which, being practically insoluble in nitric acid, separates out completely after a short time.

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CXLV.—*Geranyl Chloride.*

By MARTIN ONSLOW FORSTER and DAVID CARDWELL.

DURING an investigation of nitrosoazides from dipentene and the limonenes (T., 1911, **99**, 2059) several attempts were made to prepare a nitrosochloride of geraniol, there being no obvious reason why such a substance has not been described. Neither geraniol nor geranyl acetate combined with nitrosyl chloride, however, and attempts to produce a nitrosite or nitrosate were also fruitless. Expecting that geranyl chloride might yield such derivatives where geraniol failed, we prepared considerable quantities of this compound, and proceeded to study several geranyl derivatives, hoping to encounter one having a characteristic or agreeable perfume.

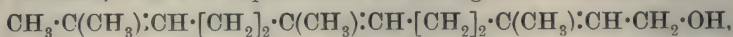
Our knowledge of the work published on this subject from other laboratories has been limited by the fact that geranyl chloride does not appear in Richter's "Lexikon," although references to the substance occur in the literature. The first of these is by Jacobsen (*Annalen*, 1871, **157**, 236), who obtained a compound, $C_{10}H_{17}Cl$, from geraniol by the action of hydrogen chloride or of hydrochloric acid at 80—90°; it is said to have D^{20} 1.020, and to have a camphor-like odour, but, although analysed, it was not distilled, because it decomposed when boiled under atmospheric pressure. Tiemann and Schmidt (*Ber.*, 1896, **29**, 921) were able to separate citronellol in the form of a hydrogen phosphite by treating a mixture of that alcohol and geraniol with phosphorus trichloride, geranyl chloride being fractionated at 98—103°/15 mm., but the latter substance was not mentioned further. Later, Tiemann (*Ber.*, 1898, **31**, 832) treated large quantities of geraniol with hydrogen chloride, and by the action of alcoholic potassium hydroxide on the product obtained a mixture of geraniol and linalool; an expressed intention to return to this subject does not appear to have been fulfilled. Dupont and Labaune (*Sci. Ind. Bull. Roure-Bertrand Fils*, 1909, [ii], **10**, 19), treating geraniol and linalool with hydrogen chloride in toluene at 100°, obtained from each alcohol the same product, which they called linalyl chloride, boiling at 95—96°/6 mm., and having D^{20} 0.9341 and n_D 1.4813; they state that the chloride produced from geraniol was not pure. Later (*loc. cit.*, 1911, [iii], **2**, 1), by means of linalyl bromide, they introduced the $C_{10}H_{17}$ -group into malonic and acetoacetic esters, whilst quite recently, Kerschbaum (*Ber.*, 1913, **46**, 1735) refers to Tigges having treated geraniol with phosphorus trichloride, and using the resulting geranyl chloride for the preparation of dihydro- ψ -ionone.

So far as we have been able to ascertain, published knowledge of geranyl chloride is limited to the foregoing facts, and we have thought it proper to summarise these because geranyl chloride is not found in the index of journals in common use.

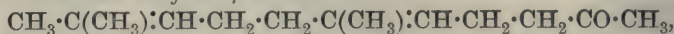
Our first step was to prepare geranyl chloride by a process which diminishes the opportunity for structural rearrangement offered by the procedure of previous workers. Adapting Darzens' method for replacing hydroxyl by chlorine, geraniol was mixed with pyridine and treated with thionyl chloride, when it yielded geranyl chloride associated with a hydrocarbon, $C_{10}H_{16}$; the former is a liquid having a marked odour of hops, and is doubtless identical with the linalyl chloride of Dupont and Labaune, since, by applying our process to linalool, the same chloride arises, and whether prepared from geraniol or from linalool, yields the same

nitrosate, $C_{10}H_{17}O_4N_2Cl$, melting at 101° , and proving a convenient material for identifying geranyl chloride. It follows from this that even by Darzens' process, as in the cruder methods of previous workers, the geranyl radicle becomes transformed into the linalyl, or vice versa. The question then arises: Has this radicle the structure of the primary geranyl nucleus, or that of the tertiary linalyl group?

We believe that this problem is solved by the recent investigation of Harries and Haarmann (*Ber.*, 1913, **46**, 1737) into the structure of farnesol, which is represented as having the constitution:



because the triozone, when decomposed with water, gives acetone and lævulinaldehyde with lævulic, acetic, and formic acids. For simultaneously, Kerschbaum (*loc. cit.*, 1735), by hydrolysing the nitrile of farnesenic acid, obtained the acid itself associated with acetic acid and dihydro- ψ -ionone:

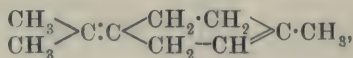


identical with a ketone we have prepared from ethyl geranylacetate (see below) and have called geranylacetone. Tigges appears to have obtained the same ketone in the same way, the description being incorporated in Kerschbaum's communication, and the substance is doubtless identical with an unnamed ketone described by Dupont and Labaune (*loc. cit.*) in an unpurified form. Now, if the substance we have named geranylacetone were linalylacetone, the constitution of farnesol would be:



from the ozonide of which lævulic acid could not arise, and it follows, therefore, that when linalool is converted into a chloride, that chloride contains the geranyl radicle. The compounds described in the present paper have been named in accordance with this principle, the assumption having been made throughout that geraniol and linalool are structurally different, as appears to follow from the work of Zeitschel (*Ber.*, 1906, **39**, 1780; 1911, **44**, 2590), Roure-Bertrand Fils (*Chem. Centr.*, 1907, ii, 464), Enklaar (*Rec. trav. chim.*, 1908, **27**, 411), and others, instead of being stereochemical isomerides, as suggested by Barbier (*Bull. Soc. chim.*, 1901, **25**, [iii], 828).

The identity of the hydrocarbon, $C_{10}H_{16}$, produced along with geranyl chloride, raises a question which we are not able to solve at present. A monocyclic terpene is suggested by its origin, and this view is confirmed by its molecular refraction, but the constitution:



that of $\Delta^{1:4(8)}$ -*p*-menthadiene, following elimination of θ -chlorine with hydrogen in the γ -position, has been assigned to terpinolene, from which our hydrocarbon appears to be different, because it yields a crystalline nitrosate melting at 131° , and is not converted into the solid tetrabromide which characterises terpinolene. Nevertheless, there is close approximation among the physical constants of our hydrocarbon and those of terpinolene as prepared by Wallach, von Baeyer, Clover (*Amer. Chem. J.*, 1907, **39**, 613), Semmler and Schossberger (*Ber.*, 1909, **42**, 4644); further experiments must be made before this point can be decided.

EXPERIMENTAL.

Geranyl Chloride (θ -Chloro- $\beta\zeta$ -dimethyl- $\Delta\beta\zeta$ -octadiene),
 $\text{CH}_3\cdot\text{C}(\text{CH}_3):\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3):\text{CH}\cdot\text{CH}_2\text{Cl}$.

One hundred grams of geraniol mixed with 50 grams of dry pyridine were externally cooled with ice and treated with 85 grams of thionyl chloride, added slowly during frequent agitation; a very vigorous action ensued, and pyridine hydrochloride separated. After being heated on the water-bath during one hour, the mixture was poured into cold water, the geranyl chloride allowed to rise in a separating funnel, washed with dilute sodium hydroxide, and dried with calcium chloride. Distillation under reduced pressure separated a more volatile material consisting of the hydrocarbon, $\text{C}_{10}\text{H}_{16}$ (see below), but this amounted to 8 grams only, whilst 65 grams of geranyl chloride were obtained:

0.1412 gave 0.1198 AgCl. $\text{Cl}=20.9$.

$\text{C}_{10}\text{H}_{17}\text{Cl}$ requires $\text{Cl}=20.6$ per cent.

Geranyl chloride is a colourless liquid with a marked odour of hops; it boils at $103^\circ/14$ mm., has D_{25}^{25} 0.918 and n_D^{25} 1.4741, whence M 52.7 (calc., $\text{C}_{10}\text{H}_{17}\text{Cl}$ \equiv 52.5).

The *nitrosate*, prepared by adding fuming nitric acid (2.5 c.c.) to geranyl chloride (2.5 grams) mixed with amyl nitrite (5 c.c.) and glacial acetic acid (6 c.c.) well cooled and stirred, separated as a white, crystalline powder. It was recrystallised by adding water to the solution in acetone, and melted with vigorous decomposition at 101° :

0.1295 gave 11.8 c.c. N_2 at 24° and 762 mm. $\text{N}=10.3$.

0.1208 „ 0.0647 AgCl. $\text{Cl}=13.2$.

$\text{C}_{10}\text{H}_{17}\text{O}_4\text{N}_2\text{Cl}$ requires $\text{N}=10.2$; $\text{Cl}=13.4$ per cent.

The substance dissolves freely in cold benzene or chloroform, crystals from which separate after adding petroleum, in which it is insoluble; it dissolves in warm methyl alcohol without developing a blue or green colour.

On repeating the foregoing experiment with linalool, the same mixture of chloride and hydrocarbon was produced, their identity with the materials derived from geraniol being established by their physical constants and by conversion into their respective nitrosates.

The Hydrocarbon, $C_{10}H_{16}$.—The lower fraction obtained in the purification of geranyl chloride was redistilled until free from chlorine, when a colourless hydrocarbon was obtained boiling at $174\text{--}176^\circ/763$ mm. and $75^\circ/14$ mm., having D^{25} 0.836 and n_D 1.4725, whence M 45.36 (calc., $C_{10}H_{16}$ 12 45.26).

0.0862 gave 0.2782 CO_2 and 0.0906 H_2O . $C=88.0$; $H=11.8$.

$C_{10}H_{16}$ requires $C=88.15$; $H=11.85$ per cent.

Many attempts have been made under varied conditions to prepare from this hydrocarbon a tetrabromide, a hydrobromide, and a nitrosochloride, but in no case was a crystalline derivative obtained. The *nitrosate*, however, separated in minute, colourless crystals within half an hour after adding fuming nitric acid (5 c.c.) to a well-cooled mixture of the hydrocarbon (4 c.c.) with amyl nitrite (10 c.c.) and glacial acetic acid (12 c.c.). After being washed with cold alcohol followed by acetone, it was recrystallised from ethyl acetate, and melted with vigorous decomposition at 131° :

0.1341 gave 13.9 c.c. N_2 at 20° and 763 mm. $N=13.1$.

$C_{10}H_{16}O_4N_2$ requires $N=13.2$ per cent.

It can be recrystallised also from glacial acetic acid.

Geranyl Ethyl Ether, $C_{10}H_{17}\cdot O \cdot C_2H_5$.

The fact that esters of geraniol are commonly materials with a pleasant odour, led us to prepare the ethyl ether in the hope that this might be a perfume, but although it has a distinctly rose-like odour, this is too faint to recommend the substance for practical purposes. Geranyl chloride (8.5 grams) was heated under reflux during one hour with alcohol (25 c.c.) in which sodium (1.2 grams) had been dissolved, when sodium chloride separated almost immediately. The ether was then precipitated with water, extracted with ether, and dried with calcium chloride:

0.1594 gave 0.4646 CO_2 and 0.1753 H_2O . $C=79.4$; $H=12.2$.

$C_{12}H_{22}O$ requires $C=79.1$; $H=12.0$ per cent.

Geranyl ethyl ether boils at $115^\circ/19$ mm., has D^{25} 0.864 and n_D 1.4662, whence M 58.3 (calc., $C_{12}H_{22}O$ 12 58.3). The substance does not yield a solid nitrosate, and although it decolorises bromine in chloroform, the product remains oily.

Hydrocarbon, C₁₀H₁₈, from Geranyl Chloride.

Ten grams of geranyl chloride suspended in 100 c.c. of 50 per cent. acetic acid were treated with 15 grams of zinc dust and heated on the water-bath during one hour; after extraction with ether and washing the solution with sodium carbonate, the dried solvent deposited a liquid free from chlorine:

0.1152 gave 0.3666 CO₂ and 0.1341 H₂O. C=86.8; H=12.9.

C₁₀H₁₈ requires C=86.95; H=13.05 per cent.

The hydrocarbon boils at 161°/763 mm. and 65°/20 mm., has D_{25}^{25} 0.768 and n_D 1.4458, whence M 47.8 (calc., C₁₀H₁₈ $\left[\begin{smallmatrix} -2 \\ 47.55 \end{smallmatrix} \right]$).

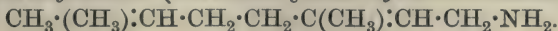
The *nitrosate* was precipitated by alcohol and water from a well-cooled mixture of the hydrocarbon (2 c.c.), glacial acetic acid (6 c.c.), and amyl nitrite (5 c.c.), to which fuming nitric acid (2.5 c.c.) had been gradually added. Recrystallisation was effected by diluting a solution in cold acetone:

0.0998 gave 10.5 c.c. N₂ at 20° and 766 mm. N=12.4.

C₁₀H₁₈O₄N₂ requires N=12.2 per cent.

The nitrosate melts and decomposes vigorously at 95°.

The constitution of the hydrocarbon should be that of $\beta\zeta$ -dimethyl- $\Delta\beta\zeta$ -octadiene, which Semmler has ascribed to dihydromyrcene (*Ber.*, 1901, **34**, 3126), obtained by reducing myrcene with sodium and alcohol. Whilst our hydrocarbon boils distinctly lower than Semmler's specimen, Enklaar's description of the physical properties (*Rec. trav. chim.*, 1907, **26**, 157) agrees closely with those observed by us, and if the identity of the two hydrocarbons is established, additional evidence will have been provided in support of our view that "geranyl chloride" contains the geranyl radicle rather than that of linalool, because Tiffeneau (*Compt. rend.*, 1908, **146**, 1153) has synthesised dihydromyrcene in such a way as to establish the constitutional formula adopted by Semmler.

Geranylamine (θ-Amino-βζ-dimethyl-Δβζ-octadiene),

Attempts to prepare geranylamine by the action of ammonia on geranyl chloride failed. The aqueous agent appeared to be without action, whilst alcoholic ammonia left much unchanged material, and produced a small proportion of a basic solid, probably consisting of digeranylamine.

Forty grams of geranyl chloride in 250 c.c. of alcohol was shaken with 24 grams of sodium azide in 80 c.c. of water during eight hours. The oil precipitated by water was suspended in 200 c.c. of glacial acetic acid mixed with 100 c.c. of water, and treated

with 50 grams of zinc dust in small quantities while the liquid was cooled and vigorously shaken. Gradually the oil dissolved with liberation of much gas, and after being warmed until effervescence ceased, the liquid was filtered and diluted with the water used to wash the unchanged zinc. In order to remove the mixture of hydrocarbon and geraniol, the solution of geranylamine acetate was extracted twice with ether before being rendered alkaline with sodium hydroxide, when a current of steam removed the base, which was isolated in the usual manner and distilled under reduced pressure, 15 grams being obtained:

0.1842 gave 15.0 c.c. N_2 at 20° and 774 mm. $N=9.7$.

$C_{10}H_{19}N$ requires $N=9.3$ per cent.

Geranylamine is a colourless liquid with a faint, musty odour; it boils at $105^\circ/19$ mm., has D^{25}_D 0.829 and n_D 1.4727, whence M 51.6 (calc., $C_{10}H_{19}N$ 51.6). Owing to the poor yield, ascribed to loss during the production of geranylazoimide, an attempt was made to prepare this by interaction of geranyl chloride and sodium azide in ether, but was unsuccessful.

The *picrate* crystallised from hot water in golden leaflets, melting at $117-119^\circ$:

0.1176 gave 15.0 c.c. N_2 at 20° and 762 mm. $N=14.9$.

$C_{10}H_{19}N, C_6H_3O_7N_3$ requires $N=14.8$ per cent.

The *hydrochloride* dissolves very freely in water, and was therefore precipitated from an ethereal solution of the base by dry hydrogen chloride. It darkens at about 100° , and melts indefinitely at 120° .

The *acetyl* derivative is a liquid boiling at $191^\circ/18$ mm.:

0.1690 gave 10.4 c.c. N_2 at 20° and 758 mm. $N=7.2$.

$C_{12}H_{21}ON$ requires $N=7.2$ per cent.

The *carbamide* separates as an oil on mixing the hydrochloride with aqueous potassium cyanate, but subsequently solidifies, and may be recrystallised from benzene or from water:

0.1343 gave 16.8 c.c. N_2 at 20° and 760 mm. $N=14.6$.

$C_{11}H_{20}ON_2$ requires $N=14.3$ per cent.

The substance dissolves sparingly in hot petroleum, and separates in the form of a gel which disintegrates to minute, silky needles, melting at 83° .

The *phenylcarbamide* remains in the form of a wax on evaporating the benzene in which geranylamine and phenylcarbimide have been mixed, but colourless crystals are deposited from petroleum, and melt at 72° :

0.1372 gave 12.3 c.c. N_2 at 20° and 760 mm. $N=10.5$.

$C_{17}H_{24}ON_2$ requires $N=10.3$ per cent.

The derivative dissolves freely in organic media, and from those which are miscible with water separates as an oil on dilution.

The benzylidene derivative is an oil, which boils at $220^{\circ}/20$ mm., and the *p*-toluenesulphonamide is also liquid.

Ethyl Geranylacetoacetate, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}(\text{C}_{10}\text{H}_{17}) \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5$.

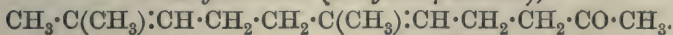
Twenty-eight grams of geranyl chloride was added to ethyl sodioacetoacetate prepared from 22 grams of the ester and 150 c.c. of alcohol in which 4 grams of sodium had been dissolved. After five hours on the water-bath under reflux, the liquid was poured into water, and the geranyl derivative extracted with ether, when 25 grams were obtained:

0.1543 gave 0.4098 CO_2 and 0.1387 H_2O . $\text{C} = 72.4$; $\text{H} = 10.0$.

$\text{C}_{16}\text{H}_{26}\text{O}_3$ requires $\text{C} = 72.2$; $\text{H} = 9.8$ per cent.

Geranylacetoacetic ester is a colourless, pleasant-smelling liquid, which boils at $180^{\circ}/16$ mm., having D_{21}^{21} 0.962 and n_D 1.4688, whence M 77.01 (calc., $\text{C}_{16}\text{H}_{26}\text{O}_3$ 76.84); it is almost certainly identical with the ester boiling at $145^{\circ}/6$ mm., prepared by Dupont and Labaune from linalyl bromide and ethyl sodioacetoacetate. On adding ferric chloride to the alcoholic solution, a purple coloration is developed.

Geranylacetone (Dihydro- ψ -ionone),



Forty grams of ethyl geranylacetoacetate, suspended in 800 c.c. of water containing 50 grams of crystallised barium hydroxide and 200 c.c. of alcohol, were heated under reflux during eight hours. On adding dilute hydrochloric acid, ether extracted 23 grams of the ketone, which boils at $139^{\circ}/19$ mm., and has n_D 1.4671/ 21° . Its identity with the material described by Kerschbaum (*Ber.*, 1913, 46, 1735) was further established by conversion into the semicarbazone, which crystallises from a mixture of benzene and petroleum in colourless plates, melting at 97° (Found, $\text{N} = 16.9$; $\text{C}_{14}\text{H}_{25}\text{ON}_3$ requires $\text{N} = 16.8$ per cent.). The phenylhydrazone, *p*-bromophenylhydrazone, oxime, and the benzoyl derivative of the last-named are all oils.

The Tertiary Alcohol, $\text{C}_{10}\text{H}_{17} \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_3)(\text{C}_6\text{H}_5) \cdot \text{OH}$.—On adding geranylacetone (12 grams) to the Grignard agent prepared from bromobenzene (12 grams) and magnesium (2 grams) in ether (150 c.c.), a vigorous action ensued, but the product remained dissolved; after being warmed during a few minutes the tertiary alcohol was isolated in the usual manner:

0.1530 gave 0.4687 CO_2 and 0.1389 H_2O . $\text{C}=83.7$; $\text{H}=10.1$.

$\text{C}_{19}\text{H}_{28}\text{O}$ requires $\text{C}=83.8$; $\text{H}=10.3$ per cent.

Homogeranylyphenylmethylcarbinol is a colourless, almost odourless liquid, boiling at $206^\circ/19$ mm. It is indifferent towards cold concentrated nitric acid, but develops a deep reddish-brown coloration with concentrated sulphuric acid.

Ethyl Geranylmalonate, $\text{C}_{10}\text{H}_{17}\cdot\text{CH}(\text{CO}_2\cdot\text{C}_2\text{H}_5)_2$.

Twenty grams of malonic ester were converted into the sodium derivative by 2.6 grams of sodium dissolved in 40 c.c. of alcohol, and heated with 25 grams of geranyl chloride during two hours under reflux. The product was treated with water, and purified in the usual manner, boiling at $191^\circ/21$ mm., having D^{21}_D 0.971 and n_D 1.4614, whence M 83.5 (calc., $\text{C}_{17}\text{H}_{28}\text{O}_4$ 83.2). It is doubtless identical with the ester prepared from linalyl bromide by Dupont and Labaune.

Geranylacetic Acid, $\text{C}_{10}\text{H}_{17}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

When geranylmalonic ester (12 c.c.) was heated on the water-bath with potassium hydroxide (10 grams) and water (10 grams) a vigorous action ensued; the homogeneous liquid was extracted once with ether, then acidified with dilute sulphuric acid and again extracted, when the solvent, having been dried with sodium sulphate, deposited a viscous liquid on evaporation. This probably consisted of geranylmalonic acid, but could not be distilled without undergoing loss of carbon dioxide, when geranylacetic acid passed over:

0.1350 gave 0.3637 CO_2 and 0.1268 H_2O . $\text{C}=73.5$; $\text{H}=10.4$.

$\text{C}_{12}\text{H}_{20}\text{O}_2$ requires $\text{C}=73.5$; $\text{H}=10.2$ per cent.

The acid is a colourless, odourless liquid, boiling at $179^\circ/19$ mm., having D^{21}_D 0.938 and n_D 1.4739, whence M 58.7 (calc., $\text{C}_{12}\text{H}_{20}\text{O}_2$ 58.4).

The sodium and silver salts are gelatinous. The *methyl* ester is a pleasant smelling, colourless liquid:

0.1557 gave 0.4230 CO_2 and 0.1484 H_2O . $\text{C}=74.1$; $\text{H}=10.6$.

$\text{C}_{13}\text{H}_{22}\text{O}_2$ requires $\text{C}=74.3$; $\text{H}=10.5$ per cent.

It boils at $160^\circ/20$ mm., and has n_D 1.4570/ 21° .

We are much indebted to Dr. J. C. Withers for valuable assistance in the opening of this investigation.

CXLVI.—*The Action of Ozone on Cellulose. Part IV. Cellulose Peroxide.*

By CHARLES DORÉE.

IN 1907 Cross and Bevan observed that cotton and linen fabrics, which had been bleached and washed with water without the use of an "antichlor," retained the property, characteristic of active oxygen, of liberating iodine from potassium iodide for a longer time than was consistent with the survival of traces of hypochlorites (*Zeitsch. angew. Chem.*, 1907, **20**, 570). Their explanation "that a peroxidised derivative of cellulose can be formed under certain conditions of the industrial bleaching process" was subsequently modified by the discovery that the hypochlorites acted on nitrogenous (protein) material present in the yarn, with the formation of chloroamine derivatives, the chlorine in which was "active" towards potassium iodide (*J. Soc. Chem. Ind.*, 1908, **27**, 260). In the course of a further study of the question, however, Ditz was able to show that a substance having the properties of a peroxide was obtained by the action of ammonium persulphate on purified cellulose (*Chem. Zeit.*, 1907, **31**, 833, 844, 857; *J. pr. Chem.*, 1908, [ii], **78**, 343). During the oxidation carbon dioxide was evolved, together with "active oxygen." This peroxide possessed the properties of a solid acid and of oxycellulose. Its activity towards potassium iodide was destroyed by gentle heating, or by boiling for a few minutes with water. The acidity was not removed by such treatment. The activity persisted for several weeks if the product was kept in a vacuum, but disappeared in two or three days if it was exposed to moist air. The amount of active oxygen fixed by the cellulose in one case amounted to 0.015 per cent.

In a previous communication on the action of ozone on cellulose (T., 1912, **101**, 504) evidence was given that ozone, in the presence or absence of water, converts cellulose into a peroxide derivative also possessing the properties of an insoluble acid. The reactions of this peroxide were found to be very similar to those of the product from ammonium persulphate. In spite of this further evidence, however, considerable doubt has always been felt as to the existence of such a derivative of cellulose. The oxidising system, in the case of ammonium persulphate, is a complex one, and both nitrogen and sulphur are present. In the case of ozone, the system is one of extreme simplicity, as it consists of cellulose and oxygen, with or without water. Here, however, the activity ascribed to a peroxide may not unfairly be considered as due to

adsorbed, or mechanically held, ozone, or to hydrogen peroxide. As the formation of a peroxide, besides being of interest in itself, would be a factor of importance in any explanation of the action of oxidising agents on cellulose, the question has been reinvestigated, the experiments being planned so as to render them as far as possible free from objection. Observations have been made on a purified cotton cellulose and extended to cellulose modified by the process of mercerising, and to the structureless cellulose obtained by regeneration from the xanthate derivative (viscose silk). The results obtained in each case point to the formation of a peroxide, and throw some light on its mode of formation and properties.

Method of Experiment.

The cotton used was a commercial second quality, not over-bleached, cotton-wool. It was purified by boiling for one hour in $N/2$ -alcoholic potassium hydroxide; then washed with dilute acetic acid and water and dried in the air. The mercerised cotton was prepared by washing the crude wool above, and then working for ten minutes in sodium hydroxide solution (D 1.3) at 14° . The viscose silk was used in the form of 120 denier threads. It was washed with acetic acid and water.

The detection and estimation of the peroxide formed depends chiefly on its power of liberating iodine from potassium iodide solution. It was found very difficult to obtain a preparation of the salt, which did not yield iodine on acidification with dilute sulphuric acid. In each case, therefore, a blank experiment was made, and a correction applied when necessary. A sample of iodide used latterly gave no liberation of iodine under the conditions employed.

The oxygen was delivered from a cylinder. It was carefully purified and dried. The concentration of the ozone was 1.5 to 2 grams per 100 grams of gas. No oxides of nitrogen could be detected. Ten litres of the gas passed into dilute alkali showed zero production of nitrates by the brucine test.

The cellulose was suspended in towers, through which the ozone was continuously passed. If necessary, sulphuric acid was placed at the bottom. After exposure, the product was placed in a desiccator, which was exhausted with a pump, a vacuum of about 1 mm. being obtained. Purified air was then admitted, and this "washing out" process repeated about six times, at intervals in the course of three days, to ensure the removal of ozone. About two grams of the material were then immersed in 100 c.c. of 10 per cent. potassium iodide solution for five minutes, after which 0.5 c.c. of 10 per cent. sulphuric acid, free from oxides of nitrogen,

was added, and the iodine immediately titrated with $N/100$ -thio-sulphate solution. The addition of acid was found to make practically no difference, as the acidity developed in the cellulose by ozone action was more than sufficient to neutralise the alkali formed in the reaction.

Quantitative Estimation of the Peroxide Activity.

In the following table are collected results obtained in this way. The material described as dry was heated for two to three hours at 102° in the case of cotton and viscose silk. The mercerised cotton was dried in a high vacuum for eight weeks, after which no further loss in weight took place. The figures given are in c.c. of $N/100$ -sodium thiosulphate solution per 100 grams of cellulose, a value which will subsequently be referred to as the "activity." The small letters indicate different preparations.

Peroxide Activity.

(C.c. $N/100$ -sodium thiosulphate solution per 100 grams.)

Time of exposure to ozone.	Cotton.		Mercerised cotton.		Viscose silk.	
	Dry	Air dry	Dry	Air dry	Dry	Air dry
1 hour	9	—	—	—	2.5	—
18 hours ...	32	{ (a) 59 (b) 70 }	47	168	32	{ (a) 269 (b) 309 }

The value 70 for cotton represents 0.0056 per cent. of active oxygen; that of 309 for viscose silk, 0.0248 per cent.

Action of Ozone on "Air Dry" Cotton, etc.

The following results were obtained with air dry material exposed for eighteen hours to ozone:

	Hygroscopic moisture.	Activity, c.c. $N/100$ -thiosulphate.	Acidity, c.c. $N/10$ -NaOH.
Cotton	6.0	70	150
Viscose silk.....	9.8	269	74

The acid substance is insoluble in water, but is neutralised and removed by alkalis. The residual fibre is neutral, and has the properties of an oxycellulose (T., 1912, 101, 506).

Properties of the Cellulose Peroxide.

(1) *Formation of Hydrogen Peroxide on Treatment with Water.*
—Preparations of cotton and viscose silk, dried at 102° , were ozonised for eighteen hours. Each product had an activity of 32 after three days' treatment in a vacuum. The viscose silk was shaken five times with small quantities of boiled, cold, distilled

water in the course of an hour. The wash water was neutral, and when tested with benzidine, copper sulphate, etc., gave no indications of the presence of ozone. On the other hand the reactions characteristic of hydrogen peroxide were well marked, notably the ferric ferri cyanide test of Schönbein, stated to be sensitive to 0.02 milligram of hydrogen peroxide per litre. That this hydrogen peroxide was produced by the action of the water on the cellulose peroxide is rendered probable by the following experiment.

2.05 Grams of the viscose silk were treated five times with water as above, and the activity of the fibre and of the water solution was estimated.

Viscose silk, original activity=32; after treatment with water, activity=15; activity of the water solution=8. Total, 23.

This loss of activity is no doubt due to the fact that the hydrogen peroxide formed reacts with the cellulose peroxide remaining with mutual decomposition.

The cotton preparation also showed a production of hydrogen peroxide, but very much less in quantity than with viscose silk. It apparently is more stable in the presence of water.

The results show that the peroxides are slowly decomposed on treatment with water, with the formation of hydrogen peroxide, a property characteristic of many organic peroxides.

(2) *The Action of Heat.*—From the following table it will be seen that whilst exposure to a temperature of 37° for two hours reduces the activity by about 25 per cent., a similar exposure at 95° destroys the activity of the cotton, but still leaves one-sixth of the activity of the viscose silk.

	Cotton (air dry).	Viscose silk (dry).	Viscose silk (air dry).
Activity, original.....	59	18	309
„ after 2 hours at 37°	48	9	220
„ „ 2 „ 95°	0	—	51

(3) *Decay of the Activity.*—When kept in the air, the activity of the products diminished slowly, and disappeared in about ten days. Thus a cotton peroxide, with an original activity of 80, showed a value of 44 after five days, and 21 after eight days. Specimens kept in a vacuum desiccator retained their activity for several weeks.

(4) *Photographic Activity.*—The products from cotton and viscose silk when fixed in close contact with the emulsion of a rapid plate were found to be very active. The material was placed on the photographic plate, covered with a sheet of glass, and the two plates held together with clips. The photographic activity was proportional to the chemical activity, namely, about five times as great with viscose silk as with cotton. With the air-dry products mentioned under (2)

a very strong printing negative was obtained in twenty days (at about 14°) with viscose silk; from the cotton in the same time the negative was good, but thin. The rate of action was enormously increased by heating. At 37° negatives of a similar density were obtained in six hours. The negative image of each thread was quite sharp, and there was no spreading of the action or fogging of the plate. Negatives made in twenty days were not so sharp as those made in six hours.*

These phenomena recall the photographic activity of the woods described by Russell (*Phil. Trans.*, 1904, **197**, 281). All the woods were found to give sharp images on a sensitive plate after three to eighteen days' exposure in the dark. At 55° negatives could be obtained in a few hours. These were very much sharper than the others. The activity was considered to be due to the slow oxidation of the resinous material present in the wood with the formation of hydrogen peroxide. A piece of resin showed the same effect as wood. The activity in both cases was stimulated by oxygen, but was inhibited by carbon dioxide.

For purposes of comparison, exposures were made (using a viscose silk of activity 300, which had been dried in a vacuum) under the following conditions: (a) in ordinary air; (b) in dry carbon dioxide; (c) in air dried by calcium chloride. The plates were also dried in a desiccator. In each case a well-exposed negative was obtained, sharp in (a) and (c), but in (b) denser and less sharp. The active substance was found to be volatile, a plate fixed 5 mm. away from the active material showing a well-marked belt of reduced silver. A glass plate 1 mm. thick prevented the action. Exposure to sunlight for two hours did not affect the activity of the preparations.

As the photographic effect is thus not dependent on the presence of water it might possibly be due to hydrogen peroxide produced during the exposure to ozone. To decide this point threads of cotton and viscose silk were treated with weak hydrogen peroxide solution and dried in a vacuum. Their activities resembled those of the viscose silk used above. Negatives obtained from them, at 37° , were, however, entirely different in character from those given by the ozonised fibres. Reduction of the silver took place in an irregular band surrounding the threads. The appearance suggested that the hydrogen peroxide volatilised from the threads, leaving them inactive, and attacked that portion of the plate which was left unscreened by the threads.

* All the plates used had a speed number, 400 H' and D. They were, in each case, developed for six minutes at 15° with a developer made up of pyrogallol, 0.15 gram, water, 30 c.c.; sodium carbonate, 10 per cent. solution, 15 c.c., sodium sulphite, 10 per cent. solution, 15 c.c.

It was also found that air-dry jute and beech wood showed no activity towards potassium iodide after exposure to ozone. An examination of the natural activity of fresh beech wood shavings by Russell's method showed that in six hours at 37° a very thin negative only was produced of about the same density as that from a cotton peroxide of activity 55.

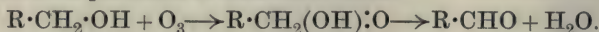
The Mechanism of the Action of Ozone on Cellulose.

With regard to the formation of peroxide by the action of ozone on cellulose, we may consider the following: (a) The ozone molecule may combine at some veiled or obscure double linking in the cellulose complex forming an ozonide.

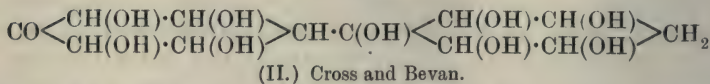
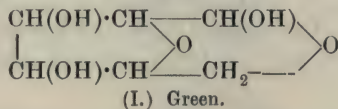
There is no evidence that any such linking exists in the cellulose complex, but it may be mentioned that ozone does combine at unsaturated linkings, the activity of which towards bromine, etc., has been inhibited by the proximity of other groupings (compare T., 1909, **95**, 640).

(b) A peroxide of the type $\text{Et}\cdot\text{O}\cdot\text{OH}$ may be formed by the combination of an atom of oxygen at a hydroxyl group.

Harries has shown (*Annalen*, 1910, **374**, 296) that ozone acting on alcohols converts them into aldehydes with the intermediate formation of a peroxide of this kind, thus:



A consideration of the following schemes, which explain many of the reactions of cellulose, shows that the alcoholic hydroxyl group-



ings might conceivably react in this way with ozone. It would appear, however, that, if so, there should be a greater proportion of oxygen combining as peroxide than was observed, unless combination took place only at some specially placed hydroxyl grouping, such as the tertiary one in formula II. The conversion to oxycellulose (aldehyde) would follow.

(c) An atom of oxygen may combine at a ring oxygen atom or at an aldehydic or ketonic carbonyl grouping forming a peroxide.

Combination might well occur at a ring oxygen atom in formula I, giving a peroxide which would decompose with the formation of aldehyde and subsequently acid. This happens with ether when

oxidised by ammonium persulphate, a diethyl peroxide and finally aldehyde being obtained.

The ketonic grouping indicated in formula II might also give a peroxide with subsequent opening of the ring and formation of aldehyde or acid. This grouping, if it exists at all, is masked in cellulose itself, but the oxycelluloses have well marked aldehydic or ketonic properties.

The fact that action takes place in the absence of water without the production of the cellulose acid, shows that, in all probability, peroxide formation alone takes place in the first instance. The peroxide oxygen attaches itself possibly at a tertiary hydroxyl group, but more probably at a carbonyl grouping. The peroxide decomposes in the presence of water, forming an aldehyde (oxycellulose), acting perhaps as a catalytic agent. This formation of aldehyde would explain too the greatly increased amount of peroxide activity observed in the presence of water. For saturated aldehydes, with ozone, readily form peroxides of the type $R \cdot CHO_2$, and these react slowly with water, giving the aldehyde again and hydrogen peroxide (for example, nonaldehyde; Harries, *loc. cit.*). The hydrogen peroxide formed would then attack the cellulose with the formation of the acid cellulose described by Bumcke and Wolffenstein (*Ber.*, 1899, **32**, 2493) as a product of the action of hydrogen peroxide on cellulose.

The reason for the greatly increased activity of mercerised cotton and viscose silk is involved no doubt in the question of the chemical relationship of these products to cellulose, as to which little is known. A series of experiments on this question is in progress, the results of which will shortly be communicated. One point may be mentioned. The regenerated cellulose yields a far higher proportion of furfuraldehyde (2 per cent.) than normal cotton (0.3 per cent.). The nature of the furfuraldehyde-yielding groupings is not known with certainty. They are generally referred to as pentosans, but they may be polyanhydrides of the kethexoses. In either case the development of additional groupings of this kind would increase the number of positions at which the combination of peroxide oxygen could take place.

The action of ozone on cellulose described above very closely resembles that of ammonium persulphate described by Ditz. From a theoretical point of view the action of ozone would resemble that of persulphate, the active oxygen in each case being of a negative character, and it would differ from that of hydrogen peroxide. Ditz ascertained that the action of the latter produced no cellulose peroxide. Both with ozone and with persulphate oxycellulose and an acid are formed, in all probability subsequently to the formation

of peroxide. Persulphates oxidise alcohols to aldehydes (Ditz, *Ber.*, 1905, **38**, 1409), and it may be that cellulose (alcohol) is converted first to oxycellulose (aldehyde). The direct formation of the acid from cellulose may find an explanation in the observation of Baeyer and Villiger (*Ber.*, 1901, **33**, 858) that ammonium persulphate acts on cyclic ketones, converting them into hydroxy-acids or their lactones with opening of the ring; thus suberone is converted into hydroxyheptoic acid, and it may be that a similar change takes place at, for instance, the $\text{CO}\cdot\text{CH}(\text{OH})$ group shown in cellulose formula II above.

According to the views of oxidation held by certain chemists, the production of hydrogen peroxide is a necessary accompaniment to the action of oxidising agents in the presence even of traces of water. It might then be urged that the properties exhibited by the ozonised cellulose are due solely to mechanically held hydrogen peroxide, and that cellulose peroxide is not formed. Against this view it may be urged:

(1) That activity is produced in the absence of water, and the active substance cannot readily be washed out from the fibres (see p. 1349).

(2) That the continued existence of hydrogen peroxide in the presence of ozone is improbable.

(3) That a similar peroxide is produced in a solution of ammonium persulphate.

(4) That the action on a photographic plate, which no doubt is due to nascent hydrogen peroxide, resembles the action of the woods (similarly explained), and differs entirely from that of cotton fibres which have been treated with hydrogen peroxide and dried.

In conclusion, I wish to express my thanks to Mr. A. Buckham for the time and skill he has given to the photographic work described in this paper.

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CXLVII.—*Note on Cupric Malate and Citrate.*

By SPENCER UMFREVILLE PICKERING.

Malate.

IN a previous communication (T., 1912, **101**, 1633) it was suggested that these two compounds, obtained as emulsions by precipitating with alcohol solutions of cupric carbonate in the acids, were really

cupri-compounds, analogous to the cupriglycerate, and not normal cupric salts, for, like the cupriglycerate, they are deeply coloured, are excessively soluble, and their behaviour on electrolysis shows that a large proportion of the copper is in the electronegative ion.

In all three cases the solutions after a time deposit crystals, but whereas in the case of the glycerate these consist of the normal salt, in the other two they consist of a basic salt, $(C_4H_4O_5Cu)_4.CuO$ and $(C_6H_5O_7)_2Cu_3.CuO$ respectively.

The difficulty in obtaining the normal salt has been overcome in the case of the malate by adding a small proportion of acid, 0.25 to 0.5 molecular proportion of malic acid for each atom of copper present. It then separates in comparatively large, hard, rhombic crystals, which seem to be quite insoluble in water, although sometimes water decomposes it into the acid salt* and the above-mentioned basic salt. It appears to retain a little water at 100° , and is slightly decomposed at 150° , becoming partly soluble, and exhibiting a green tint in solution, but the temperature of decomposition could not be determined with certainty. The mean of the values obtained at 100° and 150° , based on analyses of seven different preparations, is given below against *A*, and agrees well with that calculated for the normal malate.

The soluble cuprimalate, previously obtained by the precipitation of alcohol, was found to be not quite pure, and to yield traces of malic ether on treatment with strong acid; but the pure substance may be obtained by evaporating in a vacuum a solution of cupric carbonate in malic acid, taking only a few drops at a time. It then forms brittle, blue scales, resembling one of the cupritartrates (T., 1911, 99, 169), but of a lighter colour. It dissolves completely, and to an indefinite extent, in water, although it does not do so rapidly. There is the same doubt as to its dehydration temperature as in the case of the crystallised normal salt, but there can be no doubt that the two substances have practically the same composition. The mean results from seven different preparations of the cuprimalate, some obtained by precipitation, others by evaporation, are given against *B*.

The cuprimalate, if strictly analogous to the cupriglycerate and the majority of cupri-compounds, would contain the group $(OH)_2\overset{|}{CCu^{IV}}\overset{|}{OCO_2}$, and differ from the normal salt by H_2O ; this it does not do, and it can only be represented as a dehydrated cupri-compound, $O:\overset{|}{CCu^{IV}}\overset{|}{OCO_2}$, isomeric with the normal salt. The

* The acid salt $(C_4H_4O_5)_2CuH_2$ is fairly soluble, and is quite different from the normal malate in crystalline form.

existence of such dehydrated forms has been indicated in other cases (T., 1911, **99**, 1350).

		Percentage of copper.		Mean.
		At 100°.	At 150°.	
A.	Copper malate	31·65	33·71	32·68
B.	Cuprimalate	32·40	33·85	33·12
	Calculated	—	—	32·50

Citrate.

It was stated (T., 1912, **101**, 179) that when copper carbonate is dissolved in cold citric acid solution, and alcohol is added, an emulsion is precipitated, which, on drying at 100°, gives values corresponding with the normal salt. It is very soluble in water, and a solution of it often deposits small, hard, green crystals of the basic salt, $(C_6H_5O_7)_2Cu_6, CuO, 5H_2O$, or, in some circumstances, an anhydrous form of this salt. The nature of the crystallisation occurring from this solution has now been examined in more detail, and other products besides this basic salt have been obtained.

Attempts to obtain the normal salt by having excess of acid present, as in the case of the malate, failed, and the basic salt was still deposited when even four molecular proportions of citric acid were present to each atom of copper, although the amount deposited decreased as the proportion of acid increased.

When the dried emulsion, obtained as above, is dissolved in water (the proportions generally taken being 1·5 grams to 10 c.c.), a perfectly clear solution is obtained; but in ten minutes light blue, acicular, soft crystals begin to form, and the liquid becomes semi-solid; in another thirty minutes the mixture becomes limpid again, the first-formed crystals having changed into others, which are much smaller and squat in shape. The first crystals are perfectly soluble in water to the extent of at least 0·45 gram of copper in 100 c.c., and are still more soluble in a weak solution of citric acid; the second are soluble to the extent of not more than 0·006 gram of copper in 100 c.c., and even this amount of apparent dissolution is probably due to decomposition.

Both substances give the same results on analysis, five preparations of the first crystals and six of the second having been examined:

		At 100°.	At 150°.
First crystals		37·04	37·54
Second „		37·04	37·63

These values agree fairly well with that for a compound consisting of equimolecular proportions of the normal and ordinary

basic citrate, Cit_2Cu_3 , $\text{Cit}_2\text{Cu}_3\text{CuO}$, which would contain 36.56 per cent. of copper. Whether the small loss between 100° and 150° was accompanied by any decomposition, or not, was difficult to determine; it varied considerably, and represented, on the average, $1\text{H}_2\text{O}$ on the above formula.

The first crystals, when dried by being worked on a tile,* become greener, and after an hour are quite green, being then insoluble. A solution of them, before they are dried, deposits after a short time either the isomeric "second" substance, or the basic salt, $\text{Cit}_2\text{Cu}_3\text{CuO}$, under various conditions which have not been particularised. On one occasion the deposit consisted of a light blue, amorphous substance, containing 31.55 per cent. of copper at 100° and 150° , consisting, apparently, of the normal cupric salt, $\text{Cit}_2\text{Cu}_3 \cdot 2\text{H}_2\text{O}$, requiring 31.53 per cent. Attempts to obtain this, however, on subsequent occasions failed, so it must remain open to doubt whether the normal salt has been obtained in an insoluble form, or not; but in any case there is certainly a soluble and insoluble form of a compound consisting of equal molecular proportions of the normal and basic salts, and it seems practically certain that the very soluble substance obtained as an emulsion, which was previously termed the normal salt, is, like the corresponding malate and glycerate, a cupri-compound.

Various recent preparations of this confirmed the previous statement that its formula, after drying at 100° , was equivalent to $\text{Cit}_2\text{Cu}_3 \cdot 2\text{H}_2\text{O}$, but it appeared doubtful whether, as previously stated, it could lose $2\text{H}_2\text{O}$ at 150° without decomposition. The samples varied as to the extent of the loss, and prolonged heating at this temperature certainly resulted in some decomposition. At any rate, with only $2\text{H}_2\text{O}$, it must, like the malate, be partly dehydrated, for the non-dehydrated cupri-compound should contain $3\text{H}_2\text{O}$. Like the glycerate, it becomes partly insoluble when kept for a long time in the dry condition, and this insoluble product may be the normal cupric citrate; but it has not yet been obtained in sufficient quantity for examination.

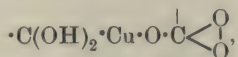
HARPENDEN.

* Some of the samples included in the mean given above were analysed without drying, and the results from them agreed well with those from the dried samples. Their composition was further verified by determining the copper and acid in solution, before and after crystallisation had occurred.

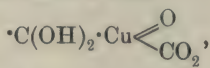
CXLVIII.—*Organic Ferric Salts.*

By SPENCER UMFREVILLE PICKERING.

THE view that the copper in the cupri-compounds is in the electronegative portion of the molecule, and that it is quadrivalent, has not found ready acceptance amongst chemists. That it is electronegative can, however, no longer be doubted; it is only necessary to electrolyse these substances in order to demonstrate that such is the case; the quadrivalent condition of the element seems to be an almost inevitable consequence of this. Taking the simplest case, such as that of the cupriglycerate, which differs from the corresponding normal salt only by the elements of one molecule of water, since the copper is in the electronegative ion, the electropositive ion *must* be hydrogen; this hydrogen can only be derived from the elements of water which have been added on to the normal salt. The formula $\cdot\text{C}(\text{OH})_2\cdot\text{O}\cdot\text{Cu}\cdot\text{O}\cdot\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\cdot$, similar to that of monohydrated copper sulphate, is unacceptable, as such a compound would, on electrolysis, give copper as the electropositive ion; the only possibilities are:



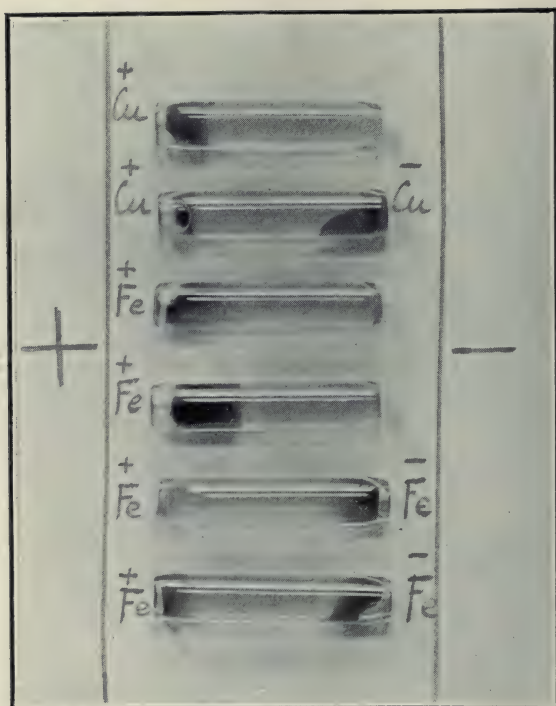
which is extremely improbable, and



with the copper quadrivalent. The latter has been found to harmonise with some fifty or sixty cupri-compounds which have been isolated, and it now receives further support from the striking similarity found between these cupri-compounds and those of quadrivalent iron.

The so-called ferric salts of organic acids, except the oxalate, form very deep-coloured solutions, from which alcohol precipitates an emulsion, and on evaporation their solutions yield the solid in a scaly form, whilst the iron in them is found to be entirely in the electronegative portion of the molecule. In all these respects they closely resemble such a compound as the cupriglycerate, and are sharply differentiated from ordinary ferric salts. Many of the ferric organic compounds are on the market, and it has long been known that they do not give the ordinary reactions of iron, but the significance of this fact does not seem to have been realised; it is quite impossible that, for instance, ferric ferrocyanide should not be formed on the addition of a ferrocyanide, if the iron is the

1258^a



[To face p. 1359.]

electropositive ion of the salt, and its not being formed* is conclusive that these salts cannot be ordinary ferric compounds. In demonstration of this, it is found that the iron on electrolysis is present as a dark brown, electronegative ion. The accompanying figure reproduces photographs of the connecting tube of gelatin used in the electrolysis apparatus in the case of copper and iron compounds. The uppermost figure shows the results with copper sulphate; here a light blue electropositive ion is observed travelling through the gelatin, but, as it is not visible in a photograph, the gelatin was impregnated with potassium ferrocyanide, and the coloured zone looks dark. The second figure gives the results with cuprimalate, and here the presence of a dark blue electronegative ion is evident; this does not react with the ferrocyanide, which was present in the gelatin tube in this case also. There is at the same time some light blue, electropositive copper (which looks dark in the photograph owing to its reaction with the ferrocyanide) moving in the opposite direction. Solutions of most cupri-compounds are partly decomposed, giving some of the normal cupric salts, but, independently of this, the presence of electropositive copper would result from acid formed by the electrolysis of the sodium chloride, which is added to the gelatin to render it conducting, this acid decomposing the cupri-compound with the formation of cupric chloride.

The results with ferric compounds are strictly similar; the third and fourth figures are those obtained with ferric chloride, with and without ferrocyanide in the gelatin, respectively, and the fifth and sixth are those obtained with the malate. Judging by the entire absence of reaction on testing the malate for iron with ordinary reagents, the electropositive iron appearing on electrolysis is solely due to the presence of the sodium chloride in the gelatin.

Similar results were obtained with the citrate, ammoniocitrate, potassic citrate, tartrate, and more questionably so with the acetate, but the oxalate gave only electropositive iron. The last two, it may also be mentioned are not precipitated by alcohol from their aqueous solutions.

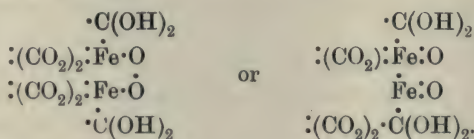
As regards their colour in solution, this appears to be of the same tint as that of ferric iron in inorganic salts, but very much more intense—the oxalate, again, being exceptional, and showing an intensity scarcely greater than that of ferric chloride. The question of colour intensity will be dealt with subsequently.

* The existing statements on this point are not very concordant. It has been found, however, that if the compound is quite neutral—which may be ensured by exposing it to ammonia gas, and heating at 100°—no trace of colour is produced by ferrocyanides, the only exceptional case being that of the oxalate, which in other respects, also, behaves like an ordinary ferric salt.

As minor peculiarities in which they resemble the cupri-compounds may be mentioned that, although they dissolve to a very great, and apparently unlimited, extent in water, most of them dissolve but slowly (like the cuprimalate, etc.), and after heating at 100° and exposure to moist air, most of them "scatter," like the scaly cupritartrate does (T., 1911, **99**, 170), so much so in the case of the ammoniocitrate that this salt cannot be weighed without special precautions.

As these compounds are not ferric salts, they must be ferri-compounds; their formula, however, cannot be identical with that of the cupri-compounds, for they contain the acid radicle and iron in the proportion of $R''_3 : Fe_2$, instead of $R''_2 : Fe$.

Formulae based on the same principle as those suggested for the cupri-compounds would be:



in one case the iron atoms being quadrivalent and not linked together; in the other, sexavalent, and united. These formulae differ from that of an anhydrous normal salt by the elements of $2H_2O$, but the difference would extend to $6H_2O$ if all the CO_2 groups became $C(OH)_2$ groups. There is no possibility of determining the proportion of constitutional water present, as the compounds dissolve very slowly after drying, and their solutions have the property of dissolving any ferric oxide which might have been liberated.*

The corresponding normal salts have not yet been obtained, as with the cupriglycerate and cuprimalate, (although, as mentioned, the oxalate is a normal salt, as also is the insoluble salicylate); but compounds with excess of ferric oxide have been prepared, both as ferri-compounds and as ferric salts, as in the case of the copper compounds with citric acid. These are represented by $R''_3Fe_2, Fe_2O_3, 6H_2O$ in the case of the tartrate, and probably by the same formula in the case of the malate (certainly so as regards the ferrimalate form of it); the citrate compounds are probably also similar, but evidence as to their composition is less satisfactory.

* For the citrate, Rieckher (*Jahrb. Chem.*, 1873, **40**, 65) gives $R'''_2Fe_2, 3H_2O$ at 100°, anhydrous at 120°; Kämmerer (*Annalen*, 1873, **170**, 186) gives $3H_2O$ as retained on the air-dried salt, and Fehling (*Neues Handw.*, II, 744) mentions (without giving references) a salt with $6H_2O$, losing $3H_2O$ at 120°, and all the water at 150°. These data are of questionable value (see below).

The Compounds $[R''_3R'''_2]Fe_2, Fe_2O_3$.

Ferri-compounds of this formula are precipitated as emulsions by the addition of alcohol to solutions of the so-called ferric tartrate, malate, or citrate, whether these are neutral, saturated with ferric hydroxide (which they dissolve in excess of that required by the formula R''_3Fe_2), or whether considerable excess of acid is present. On exposure to air, the drops of the very strong solutions which constitute these emulsions coalesce readily, the whole becoming liquid. The substances in these solutions must, of course, be highly soluble, but when dried in a vacuum—which can be done without any apparent liquefaction, if small quantities are dealt with—the resulting buff or brown powders contain, in the case of the tartrate, only a small proportion of soluble salt, and the greater part of that, even, will change into the insoluble form, if a solution of it is left for several days. The insoluble salt, which there is no reason to regard otherwise than an ordinary basic salt, is also generally obtained as a light brown, minutely crystalline deposit when a solution of the normal tartrate is left to evaporate slowly over acid, the whole mass gradually solidifying. It is obtained in larger and much darker crystals when a weaker solution is kept without evaporation for several months: the crystallisation does not start for several weeks, and if it has been kept in the light, some ferrous tartrate is eventually formed. Its solubility is 0.008 gram of iron per 100 c.c., but it is probable that this solubility is only apparent, being due to a partial transformation of it into the ferri-compound, since the iron in solution is electronegative.

The precipitated ferrimalate and ferricitrate emulsions on drying appear also to be transformed partly into the corresponding basic salts, but are reconverted into the ferri-compounds on treatment with water to a much greater extent than with the tartrate, so that quite strong, dark solutions of them are obtainable, especially with the malate, although dissolution is very slow, requiring one hour or more, the time varying considerably according to the previous treatment of the salt. Solutions of these ferri-compounds gradually deposit basic precipitates, but it has not been established that these are metameric with the corresponding ferri-compounds, as in the case of the tartrate, and they have not been obtained crystallised. On boiling, the solutions give a somewhat highly basic precipitate, which redissolves in the cool liquid after a day or two.

The experimental data are:

Eight preparations of *ferrimalate* precipitated by alcohol gave as means:

	Dried at 100°.	Dried at 130°.
Normal salt taken	28.52	30.56 per cent. Fe
Salt with excess of hydroxide	28.59	30.39 " "
" " " " acid	28.52	30.68 " "
Calc. for $R'''_3Fe_2, Fe_2O_3, 6H_2O$	28.80	— " "
" " $R'''_3Fe_2, Fe_2O_3, 3H_2O$	—	30.96 " "

In four other cases—not all cases in which excess of acid was present—lower values down to 26.1 per cent. at 100° were found. None of these approached that of the normal salt, which, even in the anhydrous condition, contains 21.94 per cent. of iron.

The *ferritartrate* showed greater variation, although not apparently connected with the presence of excess of hydroxide or acid in the solutions taken:

	Dried at 120°.
Three preparations gave values up to.....	29.7 per cent. Fe
Two " " " down to ...	23.4 " "
Seven " " " of mean ...	27.09 " "
Mean of the twelve preparations ...	27.07 " "
Calc. for $R'''_3Fe_2, Fe_2O_3, 6H_2O$	27.12 " "

The crystalline basic salt gave, as a mean for two preparations, 27.29 per cent. of iron at 120°. This temperature was selected for desiccation, as the preparations lost water very slowly indeed, and did not become satisfactorily constant, at 100°. The iron percentage on the weights at 100° were about 0.8 lower.

With the *ferricitrate* the results were unsatisfactory. The emulsion was so finely divided that filtration and washing was very difficult, a porous candle having to be used. Four preparations gave 25.74 per cent. of iron at 100° (24.8 to 26.6; this falls short of the requirements of a compound $R'''_2Fe_2, Fe_2O_3, 6H_2O$ (29.49 per cent. Fe), but is in excess of those of the normal salt, which, even if anhydrous, would contain 22.8 per cent.

Solutions of the oxalate and acetate are not precipitated by alcohol. The ferric benzoate, succinate and valerate on the market are insoluble basic salts, represented approximately by the formula $[R''_3R'_6]Fe_2, Fe_2O_3, 3H_2O$ after drying at 100°, and there is a basic acetate $(R_6Fe_2)_3Fe_2O_3$.

The Compounds $(R'_6R''_3)Fe_2$.

The existence of the scale preparations of organic ferric salts as definite compounds has been called in question by F. B. Power (*Pharm. Rundschau*, 1891, 9, 205), and his doubts seem to be justified by the antiquated and unsatisfactory state of the literature on the subject,* although evidence has now been obtained

* In several cases the statements in books of reference seem to be at variance with the evidence on which they are founded.

as to the individuality of these compounds. Attention had previously been directed chiefly to the citrate, and amongst the statements respecting it the most important is that of Rieckher (footnote, p. 1371) that some crystals were obtained agreeing fairly well with the composition $R'''_2Fe_2, 3H_2O$ at 100° . No such crystals, however, have been obtained by the present author, nor by other investigators. The difficulty is that these organic salts, just like the inorganic ferric salts, are capable of dissolving excess of ferric hydroxide, and, being uncrystallisable, evidence as to their true composition is hard to obtain. In the manufacture of them, the hydroxide and acid are taken in calculated proportions, and the product of the reaction is evaporated to a point when it will solidify when poured out on porcelain slabs.

As bearing on the behaviour of these substances, certain facts as to the inorganic salts must be notified. The chloride, nitrate and sulphate, when digested in the cold with freshly precipitated ferric hydroxide, gradually dissolve considerable quantities of it, but, after a time, the clear, dark solutions thus obtained deposit a precipitate either of ferric hydroxide in another form, or of a basic salt. With the chloride, the proportion of hydroxide which can be dissolved may reach about $20Fe_2O_3$ to each Fe_2Cl_6 , as established by previous investigators (Maus, *Pogg. Ann.*, 1827, **11**, 77; Phillips, *Phil. Mag.*, 1830, [iii], **8**, 406; Ordway, *Amer. J. Sci.*, 1868, [ii], **26**, 197; Béchamp, *Ann. Chim. Phys.*, 1859, [iii], **56**, 306; **57**, 296; Scheurer-Kestner, *Ann. Chim. Phys.*, 1862, [iii], **65**, 110; Hausmann, *Annalen*, 1854, **89**, 109; Scharizer, *Zeitsch. Kryst. Min.*, 1900, **32**, 338), but no definite limit has been obtained, and in the present experiments deposition of the insoluble hydroxide generally began long before this proportion had been reached. When, after several months, the deposition had apparently ceased, the precipitate was found to consist of pure ferric hydroxide, and the solution contained only a very small excess of iron, having the composition $33Fe_2O_3 + Fe_2Cl_6$.

By dialysing the original solution, liquids containing up to $47Fe_2O_3 + Fe_2Cl_6$ were obtained.

With the nitrate, the proportion of hydroxide dissolved reached nearly $20Fe_2O_3$ to $Fe_2(NO_3)_6$. The deposit eventually forming could not be separated satisfactorily by filtration, and was completely soluble in water. Dialysis increased the proportion to $33Fe_2O_3$ to $Fe_2(NO_3)_6$.

With the sulphate, the composition of the liquid left after deposition of the basic salt had become complete showed it to consist of $Fe_2(SO_4)_3, Fe_2O_3$ (ratio found, $Fe : SO_3 = 1 : 1.052$. Maus obtained the same ratio), but the precipitate was a basic salt of, probably,

indefinite composition, $\text{Fe}:\text{SO}_3=11:9$. On dilution of the solution, a still more basic salt, $\text{Fe}:\text{SO}_3=10:2.04$, was precipitated.

In order to examine the behaviour of organic ferric salts, precipitated ferric hydroxide was digested with the acid in various proportions at 20° until the action was complete; the quantity of hydroxide which had dissolved was then determined. The mean results of several series are given in the accompanying table, "equivalent" being used as meaning the proportion required to form a normal salt.

Ferric Hydroxide Digested with Acids.

Equivalents of Fe_2O_3 taken to 1 equivalent of acid.	Equivalents of Fe_2O_3 dissolved.		
	Tartaric acid.	Malic acid.	Citric acid.
1.0	1.00	1.00	1.00
1.1	1.009	1.088	1.098
1.25	0.857	1.184	1.230
1.5	0.632	1.248	1.180
2.0	0.406	1.264	1.086
3.0	0.153	0.861	0.744

In all three cases quantities up to one equivalent of hydroxide dissolved completely—generally in one to four days—forming dark solutions which remained permanently clear; but beyond this point, although some of the excess of hydroxide dissolved, its dissolution was accompanied by the formation of an insoluble basic salt, which, unlike the hydroxide originally taken, was pale yellow, and filtered badly. The proportion of equal equivalents of hydroxide and acid is, therefore, a point at which the character of the reaction changes, thus affording evidence of the existence of compounds of this composition. As the proportion of hydroxide taken is increased beyond our equivalent, that dissolving increases at first (although very slightly so with the tartrate), but subsequently diminishes, so much so in the case of the tartrate, that when three equivalents of hydroxide are taken, only 0.15 equivalent remains in solution. What happens is that the excess of hydroxide, or part of it, first dissolves, forming an unstable compound, which gradually changes into the metameric basic salt. The change is shown by the following determinations, wherein two equivalents of hydroxide were digested with one of tartaric acid, and gave:

After $\frac{1}{2}$ day	0.94 equivalent in solution.
„ 1 „	0.89 „ „ „
„ 2 days	0.74 „ „ „
„ 3 „	0.55 „ „ „
„ 6 to 16 days	0.20 „ „ „

An analysis of the precipitate in this case did not, however,

yield satisfactory results, due, no doubt, to there being particles of unchanged ferric hydroxide enclosed in those of the basic salt.

The results with the malate and citrate are evidently similar to those with the tartrate, but the ferri-compounds of these acids are more stable than the ferritartrate, and, consequently, more of them remains in solution. In their case an examination of the solution at various intervals of time did not give any evidence that the deposition of the basic salt was subsequent to the dissolution of the hydroxide; the two actions may, of course, follow each other so rapidly that such evidence would be unattainable. In the case of the citrate, when two equivalents of hydroxide were taken, a condition of equilibrium was reached within two days; with the malate, about twenty days were necessary.

Temperature, apparently, has little effect on the final condition of equilibrium; in all three cases, mixtures with three equivalents of hydroxide which had attained equilibrium at 20° , were heated for two hours at 100° without that condition being sensibly modified.

The behaviour of the organic ferric salts in dissolving excess of ferric hydroxide, and subsequently depositing a basic salt, is similar to that of the inorganic salts, but the excess of hydroxide which dissolves is much smaller, and it is possible that the action in the two cases may be fundamentally different, for the hydroxide dissolving in the inorganic salts is in the colloidal condition, and it is doubtful whether this is so in the case of the organic salts. The matter is being investigated; certainly, where no excess of ferric hydroxide is present, the iron in the organic salts dialyses freely, even from very dilute solutions. This dialysis, however, must be conducted in the dark, or a ferrous salt may be formed in some cases.

Ferric hydroxide was digested with acetic acid in the same way as with the other acids, but the behaviour in that case appeared to resemble that of the inorganic acids. The hydroxide dissolved in considerable quantities (2.7 equivalents), but the action was not followed to its completion, and no deposit had begun to form within ten days.

Under the heading of salts of the type $R'_6\text{Fe}_2$ may be mentioned the salicylate, which is represented by this formula after drying at 100° . It is insoluble, and is doubtless a ferric salt, not a ferri-compound.

Behaviour with Alkalis.

When an alkali is added to the ferri-compounds, $[R''_3R'''_2]\text{Fe}_2$, no precipitate is formed, and a considerable amount may be added before alkalinity is obtained. Using dilute solutions, and phenol-

phthalein as indicator, the proportion of potassium hydroxide required for alkalinity represented:

With the citrate.....	4.16K for each Fe ₂ present.
„ „ malate	5.56 „ „ „ „
„ „ tartrate	4.80 „ „ „ „
„ „ acetate	6.26 „ „ „ „

With these highly coloured solutions the reaction point cannot be determined with any certainty, but the results are not sufficiently concordant to indicate a simple and identical action in all cases. If the potassium compounds formed were analogous to the compounds R''_3Fe_2, Fe_2O_3 , the potassium hydroxide required would = 6K; this is approximately the value with the acetate and malate, but in the other cases the values are much lower. The commercial preparations of so-called potassio-ferric citrate, and analogous compounds containing ammonia or alkaloids, are of indefinite composition.

Ferric oxalate behaves differently from the ferri-compounds, an alkali causing precipitation.

Attempts to Prepare Other Ferri-compounds.

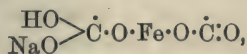
Most organic copper salts dissolve in alkalis to form cupri-compounds, and if a similar reaction occurred with ferrous salts, the ferri-compound formed should contain quadrivalent iron, although such compounds would not be the same as those discussed above, with $R''_3 : Fe_2$, which could not be formed from ferrous salts without oxidation.

That ferrous tartrate dissolves in alkalis is already known. When a strong solution of ferrous sulphate is mixed with one of sodium tartrate, the mixture gradually becomes semi-solid, owing to the formation of a white precipitate; this is minutely crystalline, moderately soluble in water, and redissolves in the liquid when warmed, being reprecipitated on cooling. If the clear, heated solution is boiled, a second white, but amorphous and denser, precipitate is thrown down. The latter is ferrous tartrate, which is anhydrous at 100°; the first precipitate is a double tartrate with the formula $4\bar{T}Fe, \bar{T}Na_2$, after drying at 100° (Found, Fe = 21.58; Na = 4.71; ratio, 2 : 1.006. Calc., $F_2 = 22.13$; Na = 4.56 per cent.).

When either of these, or the liquid containing them in the freshly precipitated condition, is mixed with sodium hydroxide, they dissolve, forming a colourless, very viscid liquid. The proportion of alkali required for dissolving the precipitate being NaOH to each Fe, indicating the formation of a compound $\bar{T}Fe, NaOH$, or $\bar{T}_2FeNa_2, NaOH$. On the addition of alcohol, the whole of the iron is precipitated as a white, flocculent, sticky mass, and this precipita-

tion also occurs when the liquid, without the addition of alcohol, is kept in a sealed tube for several days. A direct analysis of the precipitate has not been possible. It is exceedingly oxidisable, and is best manipulated under a thick layer of benzene. It dissolves in water, forming a strongly alkaline liquid, but undergoes considerable decomposition at the same time, ferrous hydroxide being separated. On oxidation the solution becomes reddish-brown, the ferritartrate (so-called ferric tartrate) being formed. With suitable precautions against oxidation, it can be proved that the iron in it is still in the ferrous condition, and when it is electrolysed (under benzene) this iron is found to be entirely electropositive. Being colourless, the ferrous ion is not visible without the addition of ferricyanide to the gelatin, but in the alkaline liquid it does not react with the ferricyanide. Its presence, however, can be recognised by immersing the gelatin tube, after the electrolysis, in weak acid for a few minutes. This affords further argument in favour of copper in the cupri-compounds being quadrivalent, for when the metal, in the case of iron, does not become quadrivalent, we find none of the other changes which characterise the action in the case of copper, namely, intense coloration and transference to the electronegative position.

The nature of the compound formed by alkalis with ferrous tartrate can only be conjectured; it may be analogous to a hydrol, containing the group:



or the alkali metal may be present in substitution of H in a CH·OH group.

A similar compound is formed in the case of the racemate, but it is decomposed by water much more rapidly than the tartrate. Attempts to obtain analogous compounds in other cases have failed, the addition of alkali to the ferrous salt precipitating ferrous hydroxide at once; an appreciable amount of iron remained in solution, however, in the case of the citrate, but traces only in that of the malate, glycollate and lactate, and none in that of the acetate, oxalate, succinate, salicylate and phthalate.

Summary.

Evidence as to the definiteness of ferric organic salts of the type $\text{R}''_3\text{Fe}_2$ is given by the dissolution of ferric hydroxide in different proportions of acid. The oxalate is a normal salt, but the tartrate, malate and citrate are ferri-compounds closely resembling the cupri-compounds; the iron is in the electronegative ion, does not give the usual reactions of iron, and possesses great colour intensity. The compounds are very soluble, and solidify in scale form. The

corresponding normal ferric salts have not been obtained in these cases. Alcohol precipitates, from their solutions, emulsions consisting of a very soluble ferri-compound of the type R''_3Fe_2, Fe_2O_3 , which change into insoluble basic salts of a similar formula. Both these metamerides are obtained in succession when the acid is digested with excess of ferric hydroxide. Their exact composition in the case of the citrate is not certain. The benzoate, succinate and valerate are basic salts of the same type, of which no corresponding ferri-metamerides have been obtained.

Ferrous organic salts do not yield ferri-compounds, as cupric salts do, with an alkali.

HARPENDEN.

CXLIX.—*The Iodocinnamic Acids.*

By THOMAS CAMPBELL JAMES.

FROM stereochemical considerations the existence of four iodocinnamic acids containing the halogen atom in the side-chain may be postulated, two α -acids, $C_6H_5 \cdot CH \cdot Cl \cdot CO_2H$, and two β -acids, $C_6H_5 \cdot Cl \cdot CH \cdot CO_2H$. At the present time three acids are mentioned in the literature, all of which are described as β -acids. The present paper describes experiments made to elucidate the constitution and configuration of these acids, and also the preparation and investigation of the fourth isomeride.

Michael (*Ber.*, 1901, **34**, 3658) describes the preparation of two iodocinnamic acids by the addition of hydrogen iodide to phenylpropionic acid in aqueous solution. By treating the product with carbon disulphide and crystallising the residue from alcohol, he obtained two acids, one described as β -iodocinnamic acid, melting at $127-128^\circ$, the other as β -iodoallocinnamic acid, melting at $187-188^\circ$. Both acids, on reducing with zinc and alcohol, yielded ordinary cinnamic acid.

The third acid was obtained by Ortoleva (*Gazzetta*, 1899, **29**, i, 504). Cinnamic acid was treated with iodine and pyridine in alcohol solution, and, on keeping, deposited a yellow, crystalline powder, melting at $165-166^\circ$, which on decomposing with 2 per cent. sodium hydroxide solution gave a small yield of an iodocinnamic acid melting at 162° . Ortoleva stated that the pyridine salt on treatment with 10 per cent. sodium hydroxide gave benzoylacetic acid, and on distillation with 2 per cent. alkali yielded acetophenone, and therefore described it as a β -iodocinnamic acid.

I.—*Preparation and Separation of Michael's Iodocinnamic Acids.*

The method described by Michael (*loc. cit.*) has been followed. Ten grams of phenylpropionic acid were gradually added to 28 c.c. of hydrogen iodide solution saturated at 10–15°, and allowed to remain in ice for a day. It was observed that under these conditions no separation of iodine took place, whereas if a solution of the acid saturated at 0° were used, copious separation of iodine occurred. The mixture was then poured into excess of water, and after filtering, the product was washed several times with water and dried on porous plate. In a series of experiments the yields obtained were as follows:

Expt. 1, 17.2 grams. Expt. 2, 18.4 grams. Expt. 3, 18.6 grams.

Separation of the product of the first experiment by the method adopted by Michael resulted in the extraction of 6.0 grams of an acid of low melting point, which after crystallisation from dilute alcohol melted at 127–128°. The residue, after crystallising from alcohol, melted at 186–188°. The amounts of the isomerides obtained are therefore in the approximate proportion of 1:2.

Attempted Separation by means of Barium Salts.—Since in the case of other halogen-substituted cinnamic acids the method of separation by means of barium salts (compare Sudborough and Thompson, T., 1903, **83**, 666) has proved effective, the method was attempted in this case also.

The barium salt of the acid melting at 127–128° consists of yellowish-white, crystalline plates:

0.3740 gave 0.1270 BaSO₄. Ba=19.99.

C₁₈H₁₂O₄I₂Ba requires Ba=20.11 per cent.

26.545 Grams of a saturated aqueous solution at 15° contained 0.4855 gram of the salt. Therefore 100 grams of water dissolve 1.863 grams of salt.

The barium salt of the acid melting at 187–188° consists of a colourless, finely crystalline powder:

0.1536, heated at 95–100° for one hour, lost 0.0160. H₂O=10.42.

0.1126 gave 0.0340 BaSO₄. Ba=17.79.

C₁₈H₁₂O₄I₂Ba.4H₂O requires H₂O=9.53; Ba=18.18 per cent.

7.9825 Grams of a saturated aqueous solution at 15° contained 0.4705 gram of salt. Therefore 100 grams of water dissolve 6.263 grams of anhydrous salt.

The solubilities of the salts are not sufficiently different to provide an effective separation.

Separation by means of Potassium Salts.—The potassium salts of *allo*-acids are, as a rule, more readily soluble in absolute alcohol than those of their stereoisomerides. A method based on this differ-

ence has been applied to the separation of the β -chlorocinnamic acids (Michael and Pendleton, *J. pr. Chem.*, 1889, [ii], 40, 65), etc.

The potassium salts of both acids have been prepared, and have been obtained as colourless, crystalline plates in each case. The solubilities in absolute alcohol have been determined.

Potassium Salt of the Acid melting at 127—128°.

6.950 Grams of a saturated solution contained 0.2640 gram of salt. 100 Grams of alcohol dissolve 3.950 grams of salt.

Potassium Salt of the Acid melting at 187—188°.

4.229 Grams of a saturated solution contained 0.6550 gram of salt. 100 Grams of alcohol dissolve 18.32 grams of salt.

The difference of solubility in this case is sufficiently great to be applied to a quantitative separation of the acids. Preliminary experiments indicated that a concentration of one part of the mixture of acids obtained in the addition experiments in 3 parts of absolute alcohol provided the best separation.

Expt. 1.—Six grams of the mixed isomerides were dissolved in alcohol, and the theoretical amount of alcoholic potassium hydroxide was added. The resulting solution was evaporated on a water-bath to a volume of 20 c.c., and allowed to remain overnight, after which the separated salt was removed and the filtrate evaporated to dryness and weighed. The sparingly soluble salt weighed 2.00 grams and the soluble salt 4.50 grams. The recovered acids melted at 126° and 186° respectively.

Expt. 2.—Ten grams of mixed acids gave 3.0 grams of the acid melting at 127—128° and 6.50 grams of the acid melting at 187—188°.

Expt. 3.—Ten grams of the mixture gave 2.7 grams and 6.9 grams respectively of the isomerides.

The results of these experiments indicate that the proportion in which the isomeric iodo-acids are formed by the addition of hydrogen iodide to phenylpropionic acid is approximately 1:2.

II.—Ortoleva's Iodocinnamic Acid.

By treating 8 grams of cinnamic acid dissolved in 4 grams of pyridine with a solution of 5 grams of iodine dissolved in 150 grams of alcohol, and allowing to remain for some time, Ortoleva (*loc. cit.*) obtained about 5 grams of a yellow salt of the composition $C_9H_7O_2I, C_5H_5N$, melting at 165—166°.

In the present investigation molecular proportions of the substances were used, with a view to examine the remaining solution.

14.8 Grams of cinnamic acid were dissolved in 15.8 grams of pyridine, and the solution was added to 25.4 grams of iodine dissolved in 300 c.c. of alcohol. After sixteen days the precipitate was collected and washed repeatedly with alcohol and ether until the washings were free from iodine. After drying, the salt weighed 15.5 grams and melted at 165° . The composition agreed with that determined by Ortoleva. (Found, $N=4.09$; $I=35.80$. Calc., $N=3.96$; $I=35.92$ per cent.)

When the proportion of iodine used in the above experiment is increased, a portion of the precipitate consisted of large, purple, crystalline prisms, which can readily be separated mechanically. These crystals have no definite melting point, but begin to decompose at 110° . The properties and composition of the substance indicate that it consists of a periodide of Ortoleva's salt. By treatment with alcohol, iodine is liberated, and by rubbing the substance with sodium thiosulphate solution in a mortar, the yellow powder melting at 165° is obtained:

0.2095 gave 0.2450 AgI. $I=63.20$.

$C_9H_7O_2I, C_5H_5N, I_2$ requires $I=62.94$ per cent.

0.2223, warmed with an aqueous solution of potassium iodide and titrated with 0.08213*N*-sodium thiosulphate solution, required 8.10 c.c.; $I=38.0$. Calc., $I=41.82$ per cent.

The mother liquors from which the above compounds separated were allowed to evaporate to dryness. After washing with sulphurous acid the residue was found to consist of cinnamic acid.

The yellow salt described above has also been prepared by the action of pyridine on β -chloro- α -iodo- β -phenylpropionic acid (compare p. 1373).

(b) *Preparation of the Acid*.—Ortoleva's observation that the pyridine salt is only partly decomposed by treatment with mineral acids has been confirmed, and the method described by him for the separation of the acid had perforce to be adopted. The pyridine salt, in portions of 2 grams, was dissolved by heating with 20 c.c. of 2 per cent. sodium hydroxide on a water-bath for three minutes. The resulting solution was filtered, acidified with sulphurous acid, and extracted with ether. The crystalline acid obtained from the ethereal extract was recrystallised from benzene, from which it separates in colourless needles melting at 162° , which become yellow on keeping. The yield from 12 grams of salt was 1.2 grams.

The potassium and ammonium salts of the acid are sparingly soluble in water, and the barium salt only very sparingly soluble. An aniline salt is obtained by dissolving the acid in benzene, adding aniline, and then precipitating the salt by addition of light petroleum. It consists of pale yellow needles, melting at 108° :

0.1800 gave 0.1180 AgI. $I=35.4$.

$C_9H_7O_2I, C_6H_7N$ requires $I=34.7$ per cent.

Stoermer and Heymann (*Ber.*, 1913, **46**, 1257) have prepared aniline salts of similar composition from α -chloro- and α -bromocinnamic acids.

III.—*Addition of Hydrogen Iodide to Phenylpropionic Acid in Non-hydroxylic Solvents.*

By the addition of hydrogen bromide to phenylpropionic acid in non-hydroxylic solvents, Sudborough and Thompson (*T.*, 1903, **83**, 1159) have obtained good yields of α -bromocinnamic acids. A number of experiments have been performed in order to ascertain the products of addition of hydrogen iodide to phenylpropionic acid under similar conditions, the solvents used being benzene, carbon disulphide, and chloroform. The best results were obtained with the first-mentioned solvent, the product consisting almost entirely of the β -iodocinnamic acid, melting at $187-188^\circ$.

IV.—*Preparation of α -Iodocinnamic Acids.*

The α -chloro- and α -bromo-cinnamic acids are prepared by an application of the reactions:

Cinnamic acid + halogen — hydrogen haloid,

the process being carried out in two stages. It has not been found possible to prepare $\alpha\beta$ -di-iodo- β -phenylpropionic acid directly from cinnamic acid, so that the general method of preparation is not applicable in this case. It is obvious, however, that the reactions entailed in the preparation of Ortoleva's pyridine salt are of the above type, so that the iodocinnamic acid melting at 162° is probably an α -iodo-acid.

β -Chloro- α -iodo- β -phenylpropionic acid was prepared according to Erlenmeyer's method (*Annalen*, 1896, **289**, 269) by the addition of iodine chloride in ethereal solution to cinnamic acid. The compound has also been obtained as follows:

A concentrated solution of chlorine was prepared by passing the dry gas into carbon tetrachloride. The strength of the solution was determined by titration with sodium thiosulphate solution. The theoretical amount of iodine was then added to a portion of the solution, and the mixture allowed to remain with occasional shaking until all the iodine passed into solution. The theoretical amount of cinnamic acid dissolved in ether was then added, and the mixture exposed to the light for two days. After removing the solvent, the product was extracted with cold chloroform (in which cinnamic acid is only sparingly soluble), and the additive compound

precipitated by addition of light petroleum. Ten grams of cinnamic acid treated in this manner yielded 15 grams, that is, 70 per cent. The substance begins to darken at 100°, and melts and decomposes at 122—123°.

By treating the substance with alcoholic potassium hydroxide, Erlenmeyer obtained α -iodo- β -ethoxy- β -phenylpropionic acid, thus proving that the iodine is in the α -position.

By treatment with aqueous potassium hydroxide the substance yields cinnamic acid only, but when decomposed by means of pyridine gives Ortoleva's pyridine salt (compare p. 1371).

Expt. 1.—Five grams of β -chloro- α -iodo- β -phenylpropionic acid were dissolved in 20 c.c. of alcohol, and 5 grams of pyridine added. After three days 3.00 grams of a yellow salt had separated, which after washing with alcohol and ether melted at 162°, and was identical in properties and composition with Ortoleva's salt. The mother liquor on treatment with hydrochloric acid released iodine and precipitated 1.20 grams of cinnamic acid (m. p. 133°).

Expt. 2.—Two grams dissolved in 5 grams of pyridine and allowed to remain for a day, deposited 1 gram of salt.

These experiments suggest that Ortoleva's salt is a pyridine salt of an α -iodocinnamic acid.

An attempt has been made to prepare $\alpha\beta$ -di-iodo- β -phenylpropionic acid from $\alpha\beta$ -dihydroxy- β -phenylpropionic acid by replacement. The latter acid was obtained as described by Fittig and Ruer (*Annalen*, 1892, **268**, 27) by the oxidation of cinnamic acid with potassium permanganate in alkaline solution.

Expt. 1.—Four grams of $\alpha\beta$ -dihydroxy- β -phenylpropionic acid were treated with 10 c.c. of a saturated solution of hydriodic acid and kept at the ordinary temperature for a fortnight, after which the mixture was poured into water, in order to separate the product from any residual dihydroxyphenylpropionic acid, which is soluble in water. A yellow precipitate was obtained, which weighed 5.0 grams, and after crystallisation from benzene melted and decomposed at 130°.

Analysis of the product showed that it was not $\alpha\beta$ -di-iodo- β -phenylpropionic acid, but an iodocinnamic acid which is obtained from the expected product by elimination of hydrogen iodide:

0.2476 gave 0.2102 AgI. $I = 45.9$.

$C_9H_7O_2I$ requires $I = 46.3$ per cent.

Further experiments showed that the best conditions for obtaining a good yield of the acid are as indicated above.

The substance decomposes on heating above the melting point, giving off iodine; decomposition also takes place when its solution in alcohol is titrated with alkalis. Like α -chloro- and α -bromo-

allocinnamic acids (Stoermer and Heymann, *loc. cit.*), it forms an acid aniline salt, which is precipitated from a solution of the acid in benzene and aniline on addition of light petroleum. This salt decomposes gradually above 120° :

0.1172 gave 0.0946 AgI. $I=43.6$.

$2C_9H_7O_2I, C_6H_7N$ requires $I=42.7$ per cent.

Therefore this acid is probably α -iodo*allocinnamic acid*.

V.—*Constitution of the Iodocinnamic Acids.*

The addition of hydrogen haloids to $\alpha\beta$ -acetylenic acids in aqueous solution usually results in the halogen being added in the β -position, so that Michael's iodocinnamic acids, melting at 127 — 128° and 187 — 188° respectively, may be classed as β -substituted acids.

Ortoleva's acid, melting at 162° , is, from the manner of its formation, an α -acid. It is, however, described as a β -acid, because the decomposition of the pyridine salt by means of 10 per cent. alkali yields benzoylacetic acid, and distillation with 2 per cent. alkali yields acetophenone. The latter result has been confirmed.

Five grams of the pyridine salt were treated with 100 c.c. of 2 per cent. sodium hydroxide, and distilled until no more oily drops passed over. The distillate was treated with hydrochloric acid to remove pyridine, and extracted with ether. The residual oil, after distilling off the ether, was treated with excess of phenylhydrazine in acetic acid solution, and gave 0.90 gram of acetophenonephenylhydrazone (m. p. 107°), that is, a 30 per cent. yield calculated from the amount of salt taken.

It may be that this decomposition is caused by the elimination of hydrogen iodide from the pyridine salt, with subsequent addition of water and decomposition of the resulting compound into acetophenone and pyridine; thus ethyl α -bromocinnamate, under the influence of sulphuric acid, forms ethyl benzoylacetate (Michael and Browne, *Ber.*, 1886, **19**, 1393). The formation of the pyridine salt from β -chloro- α -iodo- β -phenylpropionic acid affords strong evidence of an α -constitution for this acid, and this is supported by a consideration of its properties.

The acid melting at 130° is, from the manner of its formation, an α -acid.

VI.—*Stereoisomerism of the Iodocinnamic Acids.*

Michael (*loc. cit.*) describes the acid melting at 127 — 128° as β -iodocinnamic acid, and the acid melting at 187 — 188° as β -iodo*allocinnamic acid*, but the configuration implied in this nomencla-

ture is not supported by experimental evidence. An examination of the properties indicates that this nomenclature is correct, the acid of higher melting point possessing the *cis*-configuration. The acid melting at 162° is probably α -iodocinnamic acid, and that melting at 130° α -iodo*allocinnamic* acid.

Solubility of Salts.—The solubility of the barium salts in water has been applied for the separation of the chloro- and bromocinnamic acids, the salt of the *allo*-acid in each case being readily soluble, whilst that of the isomeride is only sparingly soluble. In this case the salts of the acids melting at 127 – 128° and 162° are only very sparingly soluble.

The potassium salt of *allo*-acids are generally more soluble in absolute alcohol than those of their isomerides. The salt of the acid melting at 187 – 188° is more soluble than that of the acid melting at 127 – 128° .

Transformation of *allo*-acids into their isomerides by heat could not be investigated in these cases, for the acids melting at 187 – 188° and 130° respectively are decomposed by heating above their melting points.

Transformation by Light.—*allo*-Acids under the influence of sunlight generally pass over into their isomerides.

One gram of each β -iodo-acid was exposed to bright sunlight during two months in summer. The colour of the acid melting at 187 – 188° became gradually deeper, and its melting point was lowered, whilst the acid melting at 127 – 128° was unchanged. The former was treated with 1 c.c. of cold carbon disulphide, which, when separated and evaporated, left a residue (about 0.075 gram) of a substance melting at 120 – 122° . This indicates that transformation of this acid occurs slowly.

A specimen of the acid melting at 162° kept for a year did not undergo any change of melting point.

Action of Alkali.—The acid melting at 130° is readily decomposed by alkalis, yielding phenylacetylene. The other acids yield phenylpropionic acid:

0.50 Gram of acid melting at 187 – 188° gave 0.25 gram of phenylpropionic acid (m. p. 136°).

0.50 Gram of acid melting at 127 – 128° gave 0.28 gram of phenylpropionic acid (m. p. 136°).

0.50 Gram of acid melting at 162° gave 0.20 gram of phenylpropionic acid (m. p. 136°).

The rate of elimination of hydrogen iodide by the action of potassium hydroxide in aqueous solution has been examined kinetically in the last three cases; 1/100 gram-equivalent of the acid was dissolved in two equivalents of $N/10$ -potassium hydroxide, and

aliquot portions (25 c.c.) of the resulting solution were titrated at intervals with 0.05*N*-sulphuric acid. Temperature 15°.

Melting point of acid.	$k = 1/t \cdot \tau/a(a-x)$.	K for <i>N</i> -solution.
127—128°	0.00435	2.126
187—188	0.00002155	0.0108
162°	0.0000281	0.0141

For comparison the results for other β -halogencinnamic acids are tabulated below:

	K .		K .
β -Chloro-	0.0315	β -Chloroallo-	0.00319
β -Bromo-	0.519	β -Bromoallo-	0.0139

The results indicate that the iodo-acid melting at 127—128° is β -iodocinnamic acid, and that melting at 187—188° β -iodoallo-cinnamic acid.

Esterification Constants.—The esterification constant of an acid has been proved by Sudborough and collaborators (T., 1898, **73**, 91; 1905, **87**, 1840) to afford a satisfactory criterion of the configuration of ethylenic acids. The constant has been determined for three of these acids, for methyl alcohol at 15° the method adopted being as described by Sudborough and Roberts (*loc. cit.*).

Acid.	Series.	Number of titrations.	Concen- tration of hydrogen chloride.	$1/t \log a/a-x$.		$E_{MeOH}^{15^\circ}$
				Mean.	Corr. for 0.1 HCl.	
127—128°	<i>a</i>	7	0.03332 <i>N</i>	0.005613	0.01684	0.405
	<i>b</i>	7	0.02859 <i>N</i>	0.005250	0.01836	
187—188	<i>a</i>	7	0.03332 <i>N</i>	0.008975	0.02695	0.624
	<i>b</i>	7	0.02859 <i>N</i>	0.007770	0.02718	
162°	<i>a</i>	5	0.03332 <i>N</i>	0.000891	0.00273	0.0633
	<i>b</i>	7	0.02859 <i>N</i>	0.000807	0.00277	

For comparison the values for other halogen-substituted cinnamic acids are given (Sudborough and Roberts, *loc. cit.*):

Cinnamic acid	0.937	<i>allo</i> Cinnamic acid	—
β -Chlorocinnamic acid ...	0.355	β -Chloroallocinnamic acid	0.371
β -Bromocinnamic „ ...	0.385	β -Bromoallocinnamic „	0.419
α -Chlorocinnamic „ ...	0.101	α -Chloroallocinnamic „	0.028
α -Bromocinnamic „ ...	0.075	α -Bromoallocinnamic „	0.0096

The acid melting at 162° is therefore α -iodocinnamic acid.

Affinity Constants.—The affinity constants of the acids have been determined by Ostwald's method. Since the solubility of the acids is very small a series of independent determinations have been made.

Acid melting at 128°.

<i>V.</i>	Molecular conductivity.	100 <i>m.</i>	<i>k.</i>
1024	179.8	47.6	422×10^{-6}
1024	168.4	44.5	400
1433	196.2	51.9	390
		Mean	404×10^{-6}

Acid melting at 188°.

2444	205.8	54.4	266×10^{-6}
2788	195.2	51.6	197
		Mean	231×10^{-6}

Acid melting at 162°.

1115	197.1	52.2	511×10^{-6}
1350	210.9	55.8	522
1930	226.2	60.0	474
		Mean	502×10^{-6}

Acid melting at 130°.

958	337.9	88.0	6700×10^{-6} *
1100	337.6	87.9	5800
1356	344.1	89.6	5700
1643	350.9	91.4	5900
		Mean	5800×10^{-6}

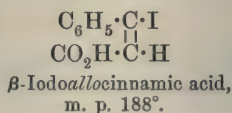
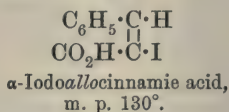
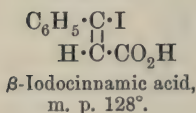
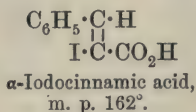
* Omitted.

For comparison the values for the cinnamic acids and their monohalogen derivatives are given in the following table:

Acid.	Affinity constant.	Determined by:
Cinnamic	35.5×10^{-6}	Ostwald (<i>Zeitsch. physikal. Chem.</i> , 1899, 3, 276).
alloCinnamic	141	Meyer (<i>Zeitsch. Elektrochem.</i> , 1911, 17, 981).
α -Chlorocinnamic	966	Mulliken (<i>Diss. Leipzig</i> , 1890).
α -Chloroallocinnamic...	10700	" " "
β -Chlorocinnamic	277	" " "
β -Chloroallocinnamic...	271	" " "
α -Bromocinnamic	930	Ostwald (<i>ibid.</i> , 278).
α -Bromoallocinnamic...	14400	" "
β -Bromocinnamic	—	
β -Bromoallocinnamic...	256	
Iodocinnamic (162°) ...	502	
" (130°) ...	5800	
" (128°) ...	404	
" (188°) ...	231	

Conclusion.

The results of the investigation indicate that the monoiodo-cinnamic acids possess the following configurations:



The author is indebted to Dr. J. J. Sudborough for his advice, and to Miss M. K. Turner for assistance in the experimental work. The expenses have been partly defrayed by a grant from the Research Fund of the Chemical Society, for which the author desires to express his thanks.

THE EDWARD DAVIES CHEMICAL LABORATORIES,
ABERYSTWYTH.

CL.—*Guanidine Thiocyanate: Its Formation from Ammonium Thiocyanate.*

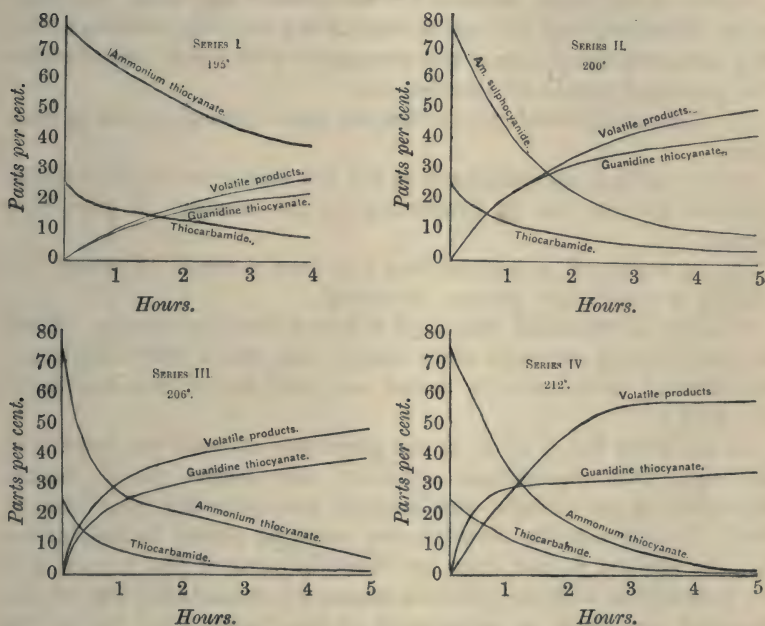
By HANS KRALL.

WHEN either dry ammonium thiocyanate or dry thiocarbamide is heated at 170° equilibrium is attained after forty-five minutes, with the formation of a mixture containing 25 per cent. of thiocarbamide and 75 per cent. of ammonium thiocyanate (Reynolds and Werner, T., 1903, **83**, 1). At this temperature a small quantity of ammonia and hydrogen sulphide is evolved, a trace of non-volatile substance is formed, but no guanidine is produced. If the temperature is raised to 180°, the formation of guanidine thiocyanate begins, with increased evolution of volatile products. The equations put forward by Volhard (*Ber.*, 1874, **7**, 92) to represent the changes that take place are purely hypothetical, and no quantitative experiments appear to have been made with a view to establish the mechanism of the change. The present work was undertaken with that object.

In order to minimise the initial formation of by-products (quite

accidental as regards the change under consideration), it seemed advisable to start all fusions with the pure equilibrium mixture artificially prepared, and consisting of 75 per cent. of ammonium thiocyanate and 25 per cent. of thiocarbamide (Expt. No. I). The use of this mixture as starting point is justified by the results given in table I. Fifteen grams of each substance named were heated in test-tubes side by side in the same bath. It will be seen that

FIG. 1.



Percentages calculated on the original mixture.

the proportions in the resulting fusion are similar, and that the volatile products are least in the case of the equilibrium mixture.

TABLE I.

One hour at 218°.

Substance heated.	Ammonium thiocyanate.	Thiocarbamide.	Equilibrium mixture.
Volatile	28.0 per cent.	30.4 per cent.	26.6 per cent.
Ammonium thiocyanate	29.6	26.3	30.4
Thiocarbamide	10.4	9.5	11.1
Guanidine thiocyanate	33.0	35.8	35.8
Ratio $\text{NH}_4\text{SCN} : \text{CSN}_2\text{H}_4$	2.84	2.77	2.74

In the experiments II—XIII (Fig. 1), which were carried out in
VOL. CIII.

order to observe the influence of temperature on the course of the reaction, the method adopted was to heat the equilibrium mixture in a series of large test-tubes immersed in an oil-bath. After successive intervals of time a test-tube was removed, the loss by volatilisation determined, and the contents were analysed as described in the experimental part. Owing to the evolution of gas, the temperature of the fusion was always below that of the bath, and was found difficult to regulate, and also a variable quantity of sublimate adhered to the sides of the tube. In these series, therefore, the individual results are only approximate, but they suffice to show clearly the comparative course of the changes. The principal points of interest are:

(1) The changes evidently follow the same general course in each series.

(2) In series I, notwithstanding the low temperature, the volatile products are no less in proportion to the amount of guanidine formed.

(3) In series IV a temperature has been reached at which the volatile products are greatly increased.

In order to establish definitely the fact that the change follows the same course, although more slowly, even below 190° , additional experiments were carefully carried out with similar results (Expt. No. XIV).

In the series No. V (Fig. 2) the procedure adopted was somewhat different. The equilibrium mixture was heated in a beaker suspended in an oil-bath, and samples were removed from time to time. In this case the thermometer could be placed in the fusion, and the method is free from the disadvantages of the former, but the quantity of volatile products cannot be estimated. The results therefore are given as percentages of the fusion, and not of the original mixture.

These curves suggest that the formation of guanidine falls off less rapidly than if the change were unimolecular, and if the velocity-constant is calculated from the equation $K = 1/t \log a/a - x$, where a is the sum of the quantities of ammonium thiocyanate and thiocarbamide, it is found that K increases in value throughout the series, thus:

Time. (in hours).	a .	$1/t \log a/a - x$.
0	87.4	—
1	55.0	0.201
2	30.0	0.233
3	10.5	0.307

Or, if the rate of formation of guanidine is taken from the slope

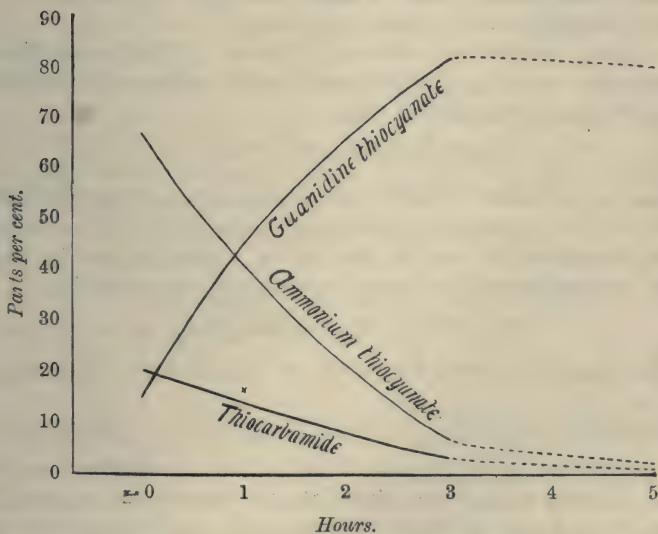
of the curve, and divided by the quantity of reacting substances present, a similar result is obtained:

Time (in hours).	<i>a</i> .	dy/dt .	$1/a \cdot dy/dt$.
1	55	1.69	0.0304
2	30	1.375	0.0458

The slowest change taking place must therefore be one which is influenced by some constant factor, such as the exposed surface, as well as by the concentration.

The volatile products were examined in a separate series of experiments, and invariably consisted of hydrogen sulphide,

FIG. 2.

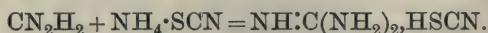


Percentages calculated on the fusion.

ammonia, carbon disulphide, and thiocyanic acid, or the interaction products of these. The quantity varied not only with the temperature and duration of heating, but with the shape of the vessel used (Expts. Nos. XXVIII and XXIX), but the constituents did not vary throughout the whole of the experiments. The ratio of nitrogen to sulphur is of little value, since guanidine thiocyanate itself evolves ammonia when heated (Expts. Nos. XXII and XXIII).

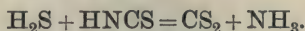
The results obtained have shown that the changes follow the same general course from 170° up to 235° , and probably higher, and it is interesting to note that the equilibrium between thio-

carbamide and ammonium thiocyanate tends to maintain itself as at the lower temperature. The results further suggest that the essential change which comes into play above 170° is the dissociation of thiocarbamide to cyanamide and hydrogen sulphide, the former then uniting with ammonium thiocyanate to produce the corresponding guanidine salt, thus:

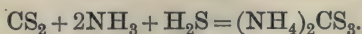


The former change agrees with the well-known union of cyanamide with hydrogen sulphide to produce thiocarbamide or with the mercaptans to produce alkyl- ψ -thiocarbamides, and accounts most easily for the large quantities of hydrogen sulphide evolved, whilst cyanamide and ammonium salts are well known to unite very readily to form guanidine salts.

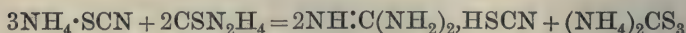
The carbon disulphide is evidently formed by the interaction of thiocyanic (or probably *isothiocyanic*) acid, produced by dissociation, and hydrogen sulphide,* thus:



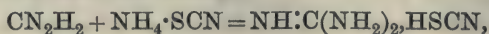
In those experiments in which the volatile products were collected, yellow crystals of ammonium trithiocarbonate were always formed, and the proportions of carbon disulphide, ammonia, and hydrogen sulphide approximated to those required by the equation:



The best single equation, therefore, to represent the whole change is:



The theoretical yield of guanidine cannot be obtained for two reasons. Firstly, owing to mass action, as the amount of guanidine increases, the chance of union of cyanamide and ammonium thiocyanate is diminished, and the very reactive cyanamide forms melamine and other related substances. Secondly, guanidine thiocyanate is not quite stable at the temperatures of experiment, the facts suggesting that the change:

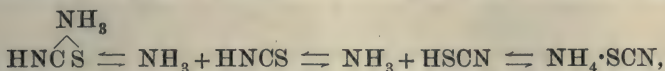


is to some extent reversible. This point is still under investigation (Expts. Nos. XXII, XXIII).

The theoretical view advanced above to account for the production of guanidine depends on the possible dissociation of thiocarbamide to cyanamide and hydrogen sulphide. Now thio-

* This reaction is attributed to Völkell (Beilstein, "Organische Chemie," Vol. I, p. 1272), but no reference is given. The reaction has, however, been verified. (Expt. XXI.)

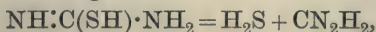
carbamide and ammonium thiocyanate, like their oxygen analogues, undoubtedly owe their interconvertibility to the reversible changes:



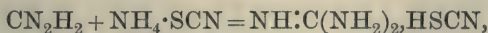
depending on the dissociation of thiocarbamide to ammonia and isothiocyanic acid (see Werner, T., 1912, **101**, 2186). The difficulty of supposing that thiocarbamide dissociates in these two ways simultaneously vanishes if we bear in mind its tautomeric nature, and there is good reason to think that at higher temperatures it tends to change partly into the isomeric form $\text{NH}:\text{C}(\text{SH}) \cdot \text{NH}_2$, which obviously ought to lose hydrogen sulphide with ease.

In agreement with this view, it has been found possible to obtain guanidine at lower temperatures by reducing the pressure (Expt. No. XXIV).

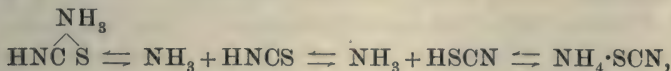
When the equilibrium mixture was heated at 190—200° in sealed tubes, guanidine was formed, and great pressure of hydrogen sulphide was developed, but little ammonia and no carbon disulphide were produced (Expt. XXV). In these conditions it is evident that the changes:



and

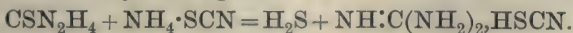


proceed, whereas the dissociation:

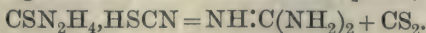


is much retarded, and hence, since little free thiocyanic acid is present, little ammonia and carbon disulphide are formed.

Thus it would seem probable that an even better yield of guanidine than that recorded below (p. 1384) could be obtained by heating in an autoclave, when the reaction might approximate to that represented by the equation:

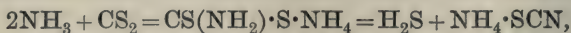


The regular and copious formation of carbon disulphide at all the experimental temperatures suggested at first that it was a primary, rather than a secondary, product of the change, and as an alternative to the explanation given, it is possible that there is transient formation of thiocarbamide thiocyanate, which might decompose into guanidine and carbon disulphide, thus:



A number of attempts to prepare this salt were made, in order to try the action of heat on it, but without success. The weight of evidence, however, is against this scheme, which would leave

the hydrogen sulphide to be accounted for by secondary changes, thus:



whereas the volatile products invariably contain very little thiocyanate, but much hydrogen sulphide. When an intimate mixture of thiocarbamide hydrochloride and potassium thiocyanate was heated, some carbon disulphide was, in fact, formed, but no guanidine could be identified; the disulphide no doubt resulted in this case from a decomposition of *isothiocyanic* acid (Expts. Nos. XXVI and XXVII).

The sparingly soluble substances formed when the equilibrium mixture is heated are mainly melamine and compounds resembling Claus's so-called thioprussamic acids (*Annalen*, 1875, **179**, 148). These will form the subject of a subsequent communication. They all suggest and confirm the ephemeral presence of free cyanamide during the reaction.

For the preparation of guanidine, the best conditions were found to consist in heating the equilibrium mixture in a narrow-necked flask at 200° for four hours, when a yield of 60 per cent. was obtained.*

No better yield can be obtained at a lower temperature to compensate for the much increased duration of heating, and at higher temperatures the sparingly soluble substances increase considerably. It is better, however, to heat too long, or to too high a temperature, than the reverse, as any unchanged ammonium thiocyanate is difficult to eliminate by recrystallisation without great loss, since ammonium and guanidine thiocyanates have a similar solubility in most solvents.

EXPERIMENTAL.

Expt. No. I.—Preparation of the Equilibrium Mixture.

Dry ammonium thiocyanate† (200 grams) was intimately mixed with the double salt, $\text{NH}_4\text{SCN} \cdot 3\text{CSN}_2\text{H}_4$ (100 grams) (Reynolds and Werner, *loc. cit.*, p. 6). The mixture was gently fused in a porcelain dish, and allowed to cool with continuous stirring until solid. While still warm, the mass was broken up and bottled. It is hygroscopic.

* Ammonium thiocyanate would generally be used instead of the equilibrium mixture; in that case, it is advisable not to raise the temperature too rapidly from 170° to 200°, in order that isomerisation may have time to take place, otherwise the loss by volatilisation is unduly increased.

† This is dried best by heating at 100° (not longer than necessary) and allowing to remain in a desiccator over solid potassium hydroxide, which removes some thiocyanic acid always produced by dissociation.

Method of Analysis.

The following procedure was invariably adopted.

The fusion was allowed to cool, and dissolved in water. If it weighed 10 to 15 grams (Series I—IV) the solution was made up to 500 c.c. When the samples removed were about 5 grams (Series V) the solution was made up to 250 c.c.

Thiocarbamide.—Ten c.c. of the solution were added to 500 c.c. of water; 5 c.c. of dilute sulphuric acid (1 in 8) added, and 4 c.c. of fresh 1 per cent. starch solution; this was titrated with *N*/10-iodine to a full blue colour (Reynolds and Werner, *loc. cit.*).

Ammonia.—Fifty c.c. of solution were boiled briskly for forty-five minutes with 300 c.c. of water and excess of ignited magnesium oxide; the distillate was led into 25 c.c. of *N*-acid, and titrated with *N*-sodium hydroxide, using methyl-orange as indicator. It was found that under these conditions all the ammonia is liberated, whilst the guanidine is not appreciably hydrolysed.

Total Thiocyanate.—Ten c.c. of the solution, with 20 c.c. of water, 5 c.c. of dilute nitric acid (1 in 8), and 25 c.c. of *N*/10-silver nitrate, were shaken in a stoppered bottle; two drops of 10 per cent. iron alum solution were then added, and the whole was titrated with *N*/10-potassium thiocyanate. This method was found better than direct titration with silver nitrate, as it is easier to observe the appearance of the pink colour than its disappearance.

The guanidine thiocyanate was determined by estimating the total thiocyanate, subtracting that due to ammonium thiocyanate, and calculating the difference to the guanidine salt. This method admittedly gives too high a result, especially in the later samples from a fusion, as other thiocyanates are present in small quantity. The error cannot be large, and in no way interferes with the general results. No better way of estimating the guanidine was devised.

Guanidine and Melamine Picrates.

Guanidine picrate crystallises in orange needles, which begin to darken at about 270°, and decompose at 285—290°, with evolution of heat; they explode if heated rapidly. At 12° the solubility is below 7 in 10,000, but in the presence of other salts it appears to be more.

Melamine, which was always formed in our experiments, gives a picrate even less soluble. It separates as a felted mass of canary-yellow needles, which darken at 240°, and become black about 300°.

In simple solution guanidine can be well estimated as picrate,

but the method was useless for our purpose (see Emich, *Monatsh.*, 1891, 12, 25).

Ethyl Acetate as a Solvent for Guanidine Thiocyanate.

It sometimes becomes necessary to separate mixtures of guanidine and ammonium thiocyanates. The solubilities of both are very similar in water, alcohol, acetone, benzene, chloroform, ether, light petroleum, or carbon disulphide. In ethyl acetate, however, the guanidine salt is not only more soluble, but enters into solution much more readily.

One hundred grams of ethyl acetate dissolve the following quantities, approximately:

Ammonium thiocyanate at the ordinary temperature	3 grams
Thiocarbamide " " "	3 "
Guanidine thiocyanate " " "	20 "
" " near boiling point of solvent.....	40 "

Guanidine thiocyanate, when crystallised from ethyl acetate, drained and washed with a little ether, is obtained colourless and pure.

Expts. II to XIII.—The Influence of Temperature.

The equilibrium mixture in samples of about 15 grams was weighed into large tared test-tubes, which were then plunged into the previously heated oil-bath, so that the required temperature might be attained by the fusion as rapidly as possible. After successive intervals a test-tube was removed, weighed, and the contents were analysed. The results are tabulated below (table II), and shown graphically in Fig. 1.

TABLE II.

Series	I.			II.			III.			IV.		
Expt. No.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.
Temperature of bath	200—204°			210°			218—225°			210—220°		
Estimated temperature of fusion	195°			200°			206°			212°		
Duration (hours)	½	2	4	1	3	5	1	3	5	1	3	5
Volatile (parts per cent.).....	6.1	18.6	27.0	21.9	42.1	42.1	34.8	42.2	46.7	28.1	56.0	57.0
Ammonium thiocyanate ..	67.6	49.9	36.5	40.3	13.8	9.4	25.6	15.1	5.6	33.9	9.0	[1.5]
Thiocarbamide..	17.8	13.1	7.7	12.5	5.4	4.3	7.5	2.5	1.4	12.1	3.1	[0.5]
Guanidine thiocyanate	5.8	16.6	22.2	22.1	36.3	41.9	27.2	34.1	38.3	29.3	31.3	34.4
Total	97.3	98.2	93.4	96.8	97.6	97.7	95.1	94.0	92.0	103.4	99.4	93.4

Expt. No. XIV.—Equilibrium Mixture Heated Below 190°.

Thirty-four grams were heated in a small retort for two hours, and the volatile products collected. A thermometer in the fusion indicated 188—190°, and the loss of weight was 17·6 per cent. The volatile portion contained all the usual substances (see Expt. No. XX), the free carbon disulphide actually collected being more than 3 per cent. of the original mixture. The fusion contained 19 per cent. of thiocarbamide (15·6 per cent. calculated on the original mixture).

In the preparation of guanidine, therefore, there is no particular point in keeping the temperature below 190°, as usually recommended.

Expts. Nos. XV to XIX.—Velocity of Reaction.

In this series the individual results are more accurate than in the earlier series. The equilibrium mixture was heated in a beaker immersed in an oil-bath, and samples of about five grams were removed, weighed, and analysed. A portion of the later samples was insoluble in cold water, and in such cases the solution was filtered before dilution to a measured volume. The volatile products could not be estimated, and the results are calculated as percentages of the fusion, not of the original mixture. The thermometer was actually in the fusion, and the mean temperature was 205°, varying between 200° and 208°. The first sample was taken when the fusion had attained 205°, and the time was reckoned from then. The results are given in table III, and shown graphically in Fig. 2.

TABLE III.

Series V.—Mean temperature of fusion, 205° (200—208°).

Temperature of bath, 215—230°.

Time (hours)	0	1	2	3	5
NH ₄ ·SCN (per cent.)	66·8	41·1	21·1	7·0	1·7
Thiocarbamide	20·6	16·6 (+)	8·7	3·5	1·0
Guanidine thiocyanate.....	15·0	45·2	65·3	81·7	80·4
Ratio NH ₄ ·SCN : CSN ₂ H ₄ ...	3·24	[2·82] *	2·44	2·01	—

* From curves.

Expt. XX.—Examination of the Volatile Products.

The equilibrium mixture was heated in a flask fitted with an inverted pear still-head, to avoid anything running back into the flask; the evolved vapours were led through a series of wash-bottles containing successively water, dilute acid, and dilute alkali. As soon as all the air had been expelled from the apparatus, the

products were completely absorbed, showing that no nitrogen was evolved. Orange crystals, which proved to be ammonium trithiocarbonate, were formed in the still-head, and carbon disulphide collected in the first wash-bottle, which also contained a trace of thiocyanate. Ammonia and hydrogen sulphide were the only other substances obtained. In various experiments at different temperatures the same products were always found. In one experiment the ratio of nitrogen to sulphur was 1.3N:1.0S (atomic ratio), but as guanidine thiocyanate itself evolves ammonia when heated, such a result is of no value, and the determination was not made in other experiments.

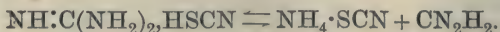
Expt. No. XXI.—Verification of Völckel's Reaction.

A current of hydrogen sulphide, dried with sodium sulphate and phosphorus pentasulphide, was led through a flask containing lead thiocyanate, and thence through a freezing mixture. When the flask was heated on the water-bath, no liquid condensed in the receiver, but when heated to a somewhat higher temperature, carbon disulphide was collected in quantity.

It is obvious that this reaction affords a simple explanation of the formation of carbon disulphide in our experiments.

Expts. Nos. XXII and XXIII.—Action of Heat on Guanidine Thiocyanate.

When this substance is heated it evolves ammonia, and, on treating the fusion with water, is found to be partly insoluble. The solution is alkaline, desulphurises slowly with alkaline solutions of lead, and after acidification decolorises iodine; with sulphuric acid it gives a precipitate of melamine sulphate. These facts suggest that the salt dissociates into cyanamide and ammonium thiocyanate, which would, of course, be partly converted in turn into thiocarbamide; in fact, that the following is a reversible reaction:



When, however, guanidine thiocyanate was heated at 170° in a current of dry hydrogen sulphide, which should combine with the cyanamide, practically no change had taken place after ten hours (titration with iodine in the usual way indicated thiocarbamide = 0.25 per cent.). It is probable that under suitable conditions guanidine thiocyanate would isomerise to guanyl thiocarbamide:



which would desulphurise and decolorise iodine like other substituted thiocarbamides. These changes are under investigation,

but for the purposes of the present communication the two following results suffice to show that, at the temperatures used above, the decomposition, although small, is appreciable.

TABLE IV.

Twenty-five grams of guanidine thiocyanate heated for three hours.

Temperature	180—185°	205—210°
Loss of weight.....	—	2·8 per cent.
Insoluble substances	1·4 per cent.	2·0 „
Thiocarbamide indicated by titration with iodine	1·0 „	1·4 „
Alkalinity in c.c. of <i>N</i> /10-acid...	22·2 c.c.	36·0 c.c.

Expt. No. XXIV.—Equilibrium Mixture Heated under Reduced Pressure.

By reducing the pressure it should be possible to form guanidine at a lower temperature. When the equilibrium mixture was heated at 173° (170—178°) for two hours under a mean pressure of 60 mm., the usual products were evolved, namely, ammonia, hydrogen sulphide, carbon disulphide, and a trace of thiocyanic acid, and the resulting fusion gave the following figures on analysis:

Ammonium thiocyanate.....	61·2 per cent.
Thiocarbamide	22·4 „
Guanidine thiocyanate	16·4 „
Ratio $\text{NH}_4\cdot\text{SCN} : \text{CSN}_2\text{H}_4$	2·73

Under atmospheric pressure no guanidine is formed at this temperature.

Expt. No. XXV.—Equilibrium Mixture Heated under Increased Pressure.

Five grams were heated in a sealed tube at 190—200° for four hours. A small quantity of sublimate was formed, consisting of ammonium trithiocarbonate. Considerable pressure was developed, and the gas proved to be mainly hydrogen sulphide, with only a trace of ammonia and no free carbon disulphide. The fusion was completely soluble in cold water, and contained no melamine; it contained 11 per cent. of thiocarbamide. The remainder consisted of the thiocyanates of ammonium and guanidine, which were not estimated.

Expt. No. XXVI.—Thiocarbamide Hydrochloride Fused with Potassium Thiocyanate.

It was hoped in this way to obtain the effect of heating thiocarbamide thiocyanate. The mixture was heated at 170° , when hydrogen sulphide and some carbon disulphide were evolved. No guanidine was found in the fusion, and much of the thiocyanic acid had polymerised.

Expt. No. XXVII.—Potassium Thiocyanate Heated in a Current of Dry Hydrogen Chloride.

When heated to 170° , polymerisation took place rapidly, and some carbon disulphide was evolved. This explains the result of the previous experiment.

Expts. XXVIII—XXX.—The Yield of Guanidine Thiocyanate under Different Conditions.

In the following table are given some results which show how the yield is affected by conditions. In these experiments it was found more satisfactory to effect a partial isolation of the products than to analyse the fusion. The method adopted was to treat the fusion with 250 c.c. of warm water, allow to remain overnight, and filter. The filtrate was evaporated as far as possible on the water-bath, and the syrupy residue (which crystallised on cooling) treated with 200 c.c. of absolute alcohol; any substance insoluble in cold alcohol was collected and the filtrate evaporated, first on the water-bath, then in an exhausted desiccator, when guanidine thiocyanate remained.

In these experiments the initial substance was 100 grams of the equilibrium mixture, and the heating was continued at the temperature named for four hours. No. XXVII indicates the best conditions. The mixture was heated in a 150 c.c. round-bottom flask with a narrow neck, immersed to the neck in an oil-bath. In No. XXIX the mixture was heated in an open beaker suspended in the oil-bath, and the temperature was slightly raised. No. XXX is inserted merely for comparison, and shows the effect of a considerably higher temperature, which is evidently to accelerate both the production and decomposition of the guanidine salt. In this experiment a flask was used, and hence the loss by volatile products is again much reduced.

TABLE V.

	XXVIII.	XXIX.	XXX.
Mean temperature of fusion ...	202° (201—204°)	208° (204—209°)	220—230°
Temperature of bath	205—211°	215—222°	
Volatile products	38 per cent.	60 per cent.	37 per cent.
Insoluble in water	trace	4·4 „	16 „
„ alcohol	0·5 „	1·0 „	5 „
Crude guanidine thiocyanate ..	60 „	33 „	40 „

In conclusion, the author desires to express his thanks to Professor E. A. Werner for his invaluable advice and criticism throughout the whole of the work.

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CLI.—*The Constitution of the ortho-Diazoimines. Part III. The α - and β -Acyl-3:4-tolylenediazoimides as Structural Isomerides.*

By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT.

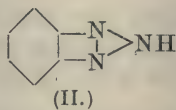
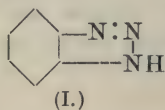
IN view of recent developments in stereochemistry, it may be anticipated that as the knowledge of molecular structure increases, the expression "physical isomerism," sometimes used to denote those anomalous cases of isomerism where it has not been found possible to give different constitutions to various modifications of what is apparently the same chemical substance, will disappear for reasons similar to those which have led to the abandonment of the term "molecular compound."

The ortho-diazoimines and their *N*-substituted derivatives furnish an example of "physical isomerism," that is, isomerism inexplicable on the basis of the current theory of the constitution of these heterocyclic substances, and this investigation was undertaken with the object of ascertaining whether an alternative hypothesis of the molecular structure of ortho-diazoimines would furnish a simple chemical explanation of the existence of the following isomerides.

By the action of nitrous acid on 4-acetyl-3:4-tolylenediamine, Bössneck (*Ber.*, 1886, **19**, 1757) prepared a diazoimino-compound, $\text{CH}_3\cdot\text{C}_6\text{H}_3\cdot[\text{N}_3]\cdot\text{CO}\cdot\text{CH}_3$, melting at 130·5°, and in the following year Zincke and Lawson, by acetylating either tolylene-3:4-diazoimine or its silver derivative, obtained a mixture of two acetyl derivatives, one of these substances (m. p. 132°) being identical

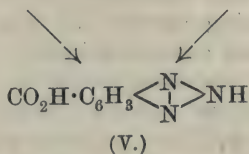
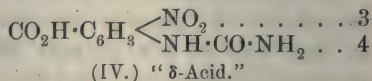
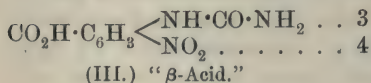
with Bössneck's compound, whereas the other was an isomeride melting at 93—94° (*Annalen*, 1887, **240**, 119).

At that time several hypotheses were extant in regard to the constitution of diazoimines. Kekulé had suggested ("Lehrbuch," II, 739) that the compounds of this series obtained by Hofmann (*Annalen*, 1860, **115**, 249) and by Ladenburg (*Ber.*, 1876, **9**, 219) were internal diazoamino-derivatives (I), which owed their existence to the contiguity of the amino-groups in the parent diamines:



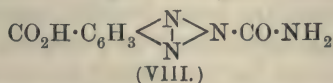
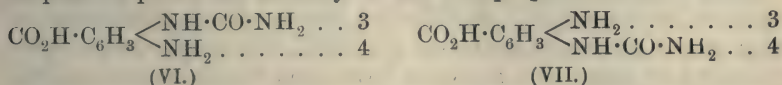
This view was adopted by Rudolph (*Ber.*, 1879, **12**, 1295), who prepared a diazoimino-derivative from *o*-aminophenylcarbamide, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$. Ladenburg assumed that the diazoimines were trisubstitution derivatives of benzene, having the formula $\text{NH}_2\cdot\text{C}_6\text{H}_3\cdot\text{N}=\text{N}$. The objections to this view are, however, too obvious to need further reference.

Two contributions by Griess to the chemistry of diazoimino-compounds led this investigator to suggest the symmetric formula (II) for these substances (*Ber.*, 1872, **5**, 192; 1882, **15**, 1878). The starting point in his researches were certain carbamido-derivatives of nitroamino- and diamino-benzoic acids (*Ber.*, 1869, **1**, 434), and it should be noticed that in one instance the supposed diazoimine was not produced by the agency of nitrous acid. By boiling with concentrated aqueous potassium hydroxide the following isomeric acids (III and IV), a complex decomposition ensued, leading to a condensation product (V), which was stated to be the same in both cases, although the methods employed for demonstrating the identity of the two preparations are not described:



These nitro-compounds (III and IV) yielded on reduction the isomeric diamino-derivatives (VI and VII), which, when treated with nitrous acid, were stated to yield the same diazoimide (VIII);

but in this instance also Griess gave no indication of the means adopted to prove the identity of the two preparations:



It can scarcely be admitted that evidence of this inconclusive character justified Griess in rejecting Kekulé's formula, and in ascribing the symmetric configuration, not only to the foregoing compounds (V and VIII), but also to all the other diazoimino-derivatives previously obtained by Hofmann, Ladenburg, and Rudolph (*loc. cit.*). Nevertheless, Griess's formulation has been more generally adopted than the dissymmetric formula put forward by Kekulé.

Zincke and Lawson (*loc. cit.*), who refer incidentally to the ill-defined character of Griess's diazoimino-derivatives (V and VIII), endeavoured to gain further evidence as to the constitution of diazoimines by a more detailed study of the two isomeric acetyl-3:4-tolylenediazoimides (see above), melting respectively at 132° and 93—94°. Hydrolysis of these isomerides led to the same 3:4-tolylenediazoimine, and by acetylating again the resulting two specimens of this compound they obtained in each case a mixture of the isomeric acetyl derivatives. Moreover, these investigators state that, contrary to Bössneck's experience, they obtained from 4-acetyl-3:4-tolylenediamine and nitrous acid, not merely the compound melting at 132°, but a mixture of this substance with the isomeride melting at 93—94°.

As the result of these experiments, they rejected Kekulé's formula for the diazoimines, and adopted that advocated by Griess. Their conclusions are best expressed in their own words (*ibid.*, p. 120):

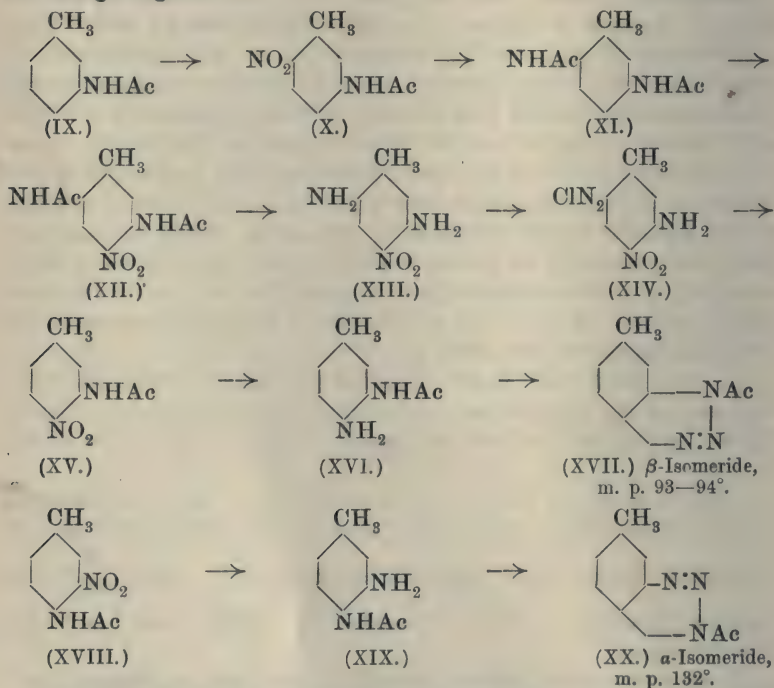
“Hiernach ist es nicht wahrscheinlich, dass die Acetylderivate chemisch verschieden sind, man wird sie als physikalisch isomer anzusehen haben und von demselben Azimid $\text{C}_6\text{H}_4 \begin{matrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{matrix} \text{NH}$ ableiten müssen. Wir unterscheiden beide also α - und β -Verbindung.”

These conclusions have apparently never been challenged, and the two substances are thus designated in the third edition of Richter's “Lexicon” (1910, p. 1224).

Recently, however, a study of the diazoimines and diazoimides of the naphthalene series has furnished considerable evidence in support of the validity of Kekulé's theory of the constitution of this group of diazo-derivatives (T., 1910, 97, 1702), and in consequence of these new facts we have been led to re-examine this alleged case of physical isomerism among benzenoid diazoimides.

Our experiments show that the α - and β -modifications of acetyl-3:4-tolylenediazoimide are true chemical isomerides, and can be obtained by methods which leave no doubt as to the orientation of the acetyl group and double linking in their respective heterocyclic rings.

A repetition of Bössneck's experiment confirmed his statement that the α -isomeride is the sole product of the action of nitrous acid on 4-acetyl-3:4-tolylenediamine (XIX). This result, which is contrary to Zincke and Lawson's statement that both isomerides are produced from this process, proves that the α -isomeride is 4-acetyl-3:4-tolylenediazoimide (XX). The synthetic production of the two isomerides is summarised in the following diagram:

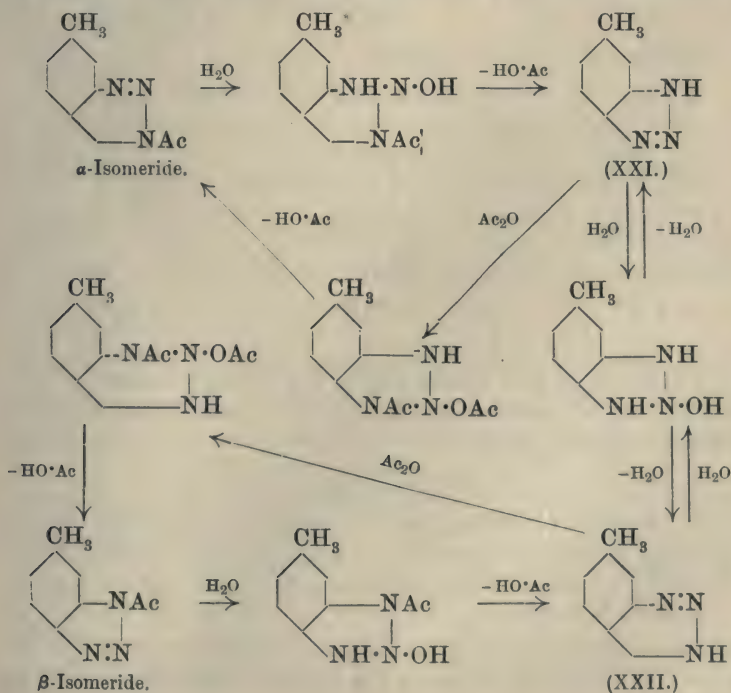


The two isomerides are hydrolysed by boiling with 50 per cent. acetic acid, and the resulting specimens of 3:4-tolylenediazoimine,

on acetylation, yield the same mixture (m. p. 108—115°) of acetyl derivatives, in which the α -isomeride predominates, since a mixture of the two compounds in equal proportions melts at about 80°.

When 3:4-tolylenediamine hydrochloride is diazotised with sodium nitrite or methyl nitrite in aqueous or alcoholic solutions, the resulting preparations of 3:4-tolylenediazoimine yield, on acetylation, similar mixtures of α - and β -isomerides, in which again the former predominates.

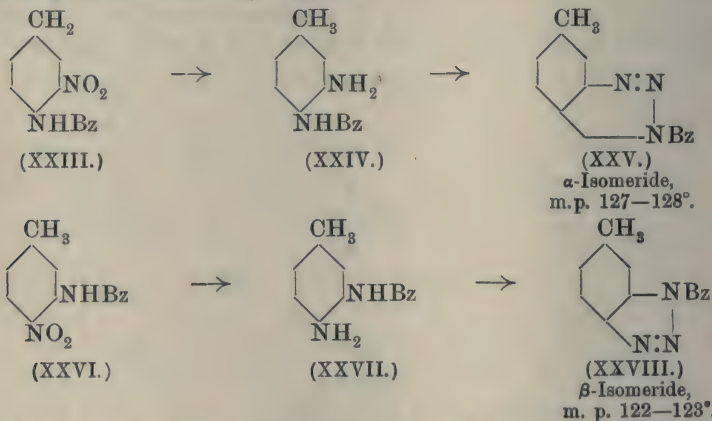
The absorption spectra of the two isomerides show distinct differences, the β -compound exhibiting selective absorption at somewhat greater dilution than its isomeride, and having a shallow band, which, with the α -compound, is reduced to a step-out and shifted towards the red end of the spectrum. The extinction curve of the mixture obtained on acetylating 2:3-tolylenediazoimine confirms the melting-point experiments in indicating a preponderance of the α -isomeride; it has in the main a form similar to the curve of the α -compound, and is situated closer to this curve than to that of the β -compound. These results indicate that isomeric change occurs both in hydrolysing the isomeric acetyl compounds and in acetylating 3:4-tolylenediazoimine. The shifting of the double bond in the triazole ring is easily explained by



assuming in the foregoing reactions respectively the addition of water and acetic anhydride, followed by the removal of acetic acid from the hypothetical additive products. These changes, which are quite comparable with those already observed in the case of certain naphthylenediazoimine derivatives (T., 1910, **97**, 1705), may be summarised as indicated in the scheme on p. 1395.

Although in the crystalline state, 3:4-tolylenediazoimine (m. p. 83–84°) may exist entirely in the less soluble of the two forms XXI and XXII, yet as produced in solution during hydrolysis of either of the two isomerides it consists of an equilibrium mixture of the two forms from which both isomerides are produced on acetylation in proportions which are fairly constant. These two isomerides show no tendency to change into each other when dissolved in the ordinary organic media, a mixture of the two being stable in all proportions.

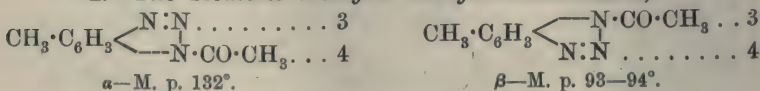
The chemical nature of the isomerism exhibited by the acetyl derivatives of 3:4-tolylenediazoimine has been confirmed by the preparation of a similar pair of benzoyl derivatives by processes indicated in the following diagram:



It is noteworthy that in this pair of isomerides the melting points differ by only 5°, whereas in the case of the acetyl derivatives the difference amounts to 38°.

EXPERIMENTAL.

I.—The Isomeric Acetyl-3:4-tolylenediazoimides,



Aceto-*p*-toluidide (1 part) was added to cooled nitric acid (D 1.47, 3 parts), and after three hours the solution was poured on to ice,

when 3-nitroaceto-*p*-toluidide separated. After crystallisation from light petroleum this nitro-compound was obtained in lemon-yellow needles, softening at 94° and melting at 96° (compare Schraube and Romig, *Ber.*, 1893, **26**, 579; m. p. 92°). The reduction of this material was conveniently effected in 50 parts of water containing 1 part of acetic acid by means of iron filings (2 parts) slowly added to the boiling solution. After neutralising with sodium carbonate the mixture was extracted with chloroform, when 4-acetyl-3:4-tolylenediamine (m. p. 110 — 112°) separated from the concentrated extract. Crystallisation from benzene raised the melting point to 130° , but this decrease in fusibility was probably due to the formation of the anhydro-base, ethenyl-3:4-tolylenediamine. This base, which was produced when the foregoing reduction was carried out in smaller quantities of water, melted at 203° .

4-Acetyl-3:4-tolylenediazoimide (Formula XX).

This diazoimide separated as a colourless, crystalline precipitate on adding aqueous sodium nitrite to a solution of 4-acetyl-3:4-tolylenediamine in *N*-acetic acid. It can be prepared equally readily in the presence of dilute mineral acids. The product, which was homogeneous, crystallised either from water or petroleum and melted at 132° :

0.1522 gave 31.3 c.c. N_2^* at 13° and 748 mm. $N=24.12$.

$C_9H_9ON_3$ requires $N=24.00$ per cent.

This compound, which is evidently identical with Zincke and Lawson's α -isomeride, was the only product of the action of nitrous acid on 4-acetyl-3:4-tolylenediamine. When crystallised from light petroleum it was frequently obtained in acicular prisms about 2 cm. in length, sometimes having a pink tinge. The compound is volatile in steam or in alcohol vapour, and has an agreeable, pungent odour resembling that of liquorice.

Preparation of 4-Nitro-m-toluidine. (1) *From 6-Nitro-m-toluidine.*

The nitration of *m*-toluidine is stated to yield 6-nitro-*m*-toluidine and three other isomerides volatile in steam, including 4-nitro-*m*-toluidine (Noelting and Stoecklin, *Ber.*, 1891, **24**, 564). On repeating this experiment several times we were not able to isolate from the volatile product any considerable amount of pure 4-nitro-*m*-toluidine. Nitration of either purified or commercial *m*-toluidine gave 6-nitro-*m*-toluidine as the main product (non-volatile in steam; m. p. 138 — 140° . Found, $N=18.44$. Calc.,

* The nitrogen in this and the following estimations was measured over 50 per cent. potassium hydroxide.

N=18.42 per cent.), accompanied by a more fusible red substance (m. p. 80—90°), the two compounds being separated by alcohol, in which 6-nitro-*m*-toluidine is more soluble.

The nitration of *m*-toluidine was carried out according to Noelting and Stoecklin's method, and the recrystallised 6-nitro-*m*-toluidine (6 parts) was suspended in hot water (100 parts) containing acetic acid (5 parts), and reduced with iron filings (10 parts). The solution of 2:5-tolylenediamine was neutralised with sodium carbonate, filtered from iron oxide, rendered slightly acid with acetic acid, and treated, whilst still warm, with excess of acetic anhydride. Providing that the liquid was sufficiently warm, a vigorous reaction sets in, and diacetyl-2:5-tolylenediamine separated on cooling in pale brown crystals (m. p. 220°).

4-Nitrodiacetyl-2:5-tolylenediamine (Formula XII).

Diacetyl-2:5-tolylenediamine (6 grams) dissolved in glacial acetic acid (25 grams) and nitrated with decolorised nitric acid (D 1.47, 3 grams) diluted with an equal volume of glacial acetic acid, yielded a colourless precipitate separating from the acid solution and very sparingly soluble in the ordinary solvents. When crystallised from glacial acetic acid, 4-nitrodiacetyl-2:5-tolylenediamine separated in well-defined, short, pale yellow prisms, melting and decomposing at 258°. This nitration proceeds satisfactorily with just sufficient cooling to moderate the reaction.

4-Nitro-2:5-tolylenediamine (Formula XIII).

When finely ground the preceding compound (5 grams) dissolved on boiling in alcoholic hydrochloric acid (30 c.c.) to a clear red solution, which speedily deposited the yellow hydrochloride of 4-nitro-2:5-tolylenediamine, the precipitation being completed by passing dry hydrogen chloride into the solution. The base set free by ammonia crystallised from hot water in needles exhibiting in different crystallisations very varying shades of colour ranging from bright red to dark green with a bronzy reflex; it softened at 170° and melted at 173°:

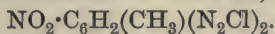
0.1194 gave 25.0 c.c. N₂ at 13° and 771 mm. N=25.32.

C₇H₉O₂N₃ requires N=25.14 per cent.

The diazotisation of 4-nitro-2:5-tolylenediamine yielded mainly the monodiazonium salt. The base was dissolved in absolute alcohol, the red solution was saturated with hydrogen chloride, and then treated with a current of methyl nitrite evolved by dropping concentrated aqueous sodium nitrite into a solution of 50 per cent. sulphuric acid in methyl alcohol (W. M. Fischer and Steinbach, *Zeitsch. anorg. Chem.*, 1912, **78**, 134).

4-Nitro-3-aminotoluene-6-diazonium chloride (formula XIV) separated in lustrous, orange-yellow leaflets dissolving in concentrated hydrochloric acid to a colourless solution; it was a very stable diazo-derivative, and required long boiling in absolute alcohol before the elimination of the diazonium group was complete. After evaporating the greater part of the alcohol, the residual solution was diluted with water until a yellow precipitate was obtained, which, when crystallised from water in the presence of animal charcoal, gave pure 4-nitro-*m*-toluidine, sintering at 109° and melting at 112°, instead of at 109°, the melting point previously indicated (Städel and Kolb, *Annalen*, 1890, **259**, 224).

The alcoholic filtrate from the diazonium chloride after boiling yielded, besides undiazotised nitrodiamine and tarry products, a compound (not identified) melting at 208—210°, and an appreciable amount of *p*-nitrotoluene (m. p. 58°). The presence of the last compound points to the existence in the original alcoholic solution of 4-nitrotoluene-2:5-bisdiazonium chloride,



A smoother reaction was brought about by triturating 4-nitro-2:5-tolylenediamine with glacial acetic acid saturated with hydrogen chloride, and adding to the creamy mass a slight excess of powdered sodium nitrite. The colour and consistence of the diamine hydrochloride changed, and a bulky precipitate of the lustrous, orange-yellow aminodiazonium chloride was produced. When boiled with absolute alcohol this salt yielded 4-nitro-*m*-toluidine (m. p. 112°), which was obtained after evaporating off the greater part of the solvent and adding acidified water to retain in solution the unaltered diamine. The yield of 4-nitro-*m*-toluidine was not more than 30 per cent. on the weight of diamine, 25 per cent. of which was usually recovered on neutralising with ammonia the mother liquor from the nitromonamine. The final filtrates when distilled in steam furnished *p*-nitrotoluene.

(2) *From o-Toluidine.*—Aceto-*o*-toluidide when added to cold concentrated nitric acid (D 1.47) yielded 5-nitroaceto-*o*-toluidide, which on reduction with iron filings and water containing a little acetic acid gave 2-acetyl-2:5-tolylenediamine. The latter compound when acetylated in aqueous solution with acetic anhydride furnished diacetyl-2:5-tolylenediamine, which was converted into 4-nitro-*m*-toluidine (m. p. 112°), as in the foregoing method. This process was abandoned because the nitration of aceto-*o*-toluidide was uncertain, and sometimes led to the production of 4-nitroaceto-*o*-toluidide, even when the experimental conditions had not been intentionally modified.

(3) *From Aceto-m-toluidide.*—*m*-Toluidine acetylated with glacial

acetic acid containing a small proportion of acetic anhydride yielded aceto-*m*-toluidide, which after crystallisation from water melted at 65°.

Contrary to earlier statements (Beilstein and Kuhlberg, *Annalen*, 1871, **158**, 348), Cohen and Dakin (T., 1903, **83**, 333) showed that the nitration of aceto-*m*-toluidide yielded principally 6-nitroaceto-*m*-toluidide, and as the reaction takes place without the formation of tarry products, aceto-*m*-toluidide is a convenient starting point in the preparation of 4-nitro-*m*-toluidine. The nitration was effected in cooled nitric acid (D 1.47); the crude product poured on to ice melted at 100°, and after repeated crystallisation from alcohol and benzene at 109°. Hydrolysis with boiling alcoholic potassium hydroxide yielded 6-nitro-*m*-toluidine (m. p. 138—140°). The acetyl compound in the mother liquors from 6-nitroaceto-*m*-toluidine gave on hydrolysis crude 4-nitro-*m*-toluidine, the yield being 10—12 per cent., in addition to which the pure base was obtained by the following series of operations.

6-Nitroaceto-*m*-toluidide, when reduced with iron filings and acidified water, yielded 5-acetyl-2:5-tolylenediamine, which on treatment in aqueous solution with acetic anhydride gave a precipitate of diacetyl-2:5-tolylenediamine (formula XI), from which, by the processes of method 1, 4-nitrodiaetyl-2:5-tolylenediamine, 4-nitro-2:5-tolylenediamine, and 4-nitro-*m*-toluidine (formulae XII and XIII) can be successively prepared.

4-Nitroaceto-*m*-toluidide (formula XV) was obtained by acetylating 4-nitro-*m*-toluidine with glacial acetic acid containing acetic anhydride or preferably acetyl chloride; it crystallised from water or petroleum in yellow needles melting at 88—89°.

3-Acetyl-3:4-tolylenediamine (formula XVI) was prepared by reducing the preceding compound (1 gram) with iron filings (1.5 grams) and water (85 c.c.) containing acetic acid (1 c.c.). After boiling for thirty minutes the solution was rendered alkaline and extracted with chloroform. This extract was concentrated and treated with petroleum, when 3-acetyl-3:4-tolylenediamine separated in nodular aggregates, which melted indefinitely at 95°. Recrystallisation from anhydrous solvents, such as benzene and petroleum, led to the elimination of water, owing to the formation of anhydro-base, this change being accompanied by a rise of melting point to 145—150°.

3-Acetyl-3:4-tolylenediazoimide (Formula XVII).

This isomeric diazoimide was produced by adding aqueous sodium nitrite to a dilute acid (acetic or hydrochloric) solution of 3-acetyl-3:4-tolylenediamine, when it separated in an amorphous

state, which rapidly redissolved, and then crystallised in colourless needles melting at 91° :

0.1234 gave 25.2 c.c. N_2 at 17° and 764 mm. $N = 24.00$.

$C_9H_9ON_3$ requires $N = 24.00$ per cent.

This compound, which is evidently identical with Zincke and Lawson's β -isomeride, is the sole product of the action of nitrous acid on 3-acetyl-3:4-tolylenediamine. When recrystallised from light petroleum it separated in well-defined, transparent, pale yellow, monoclinic prisms, melting at 93 — 94° after sintering slightly at 85 — 86° . Like the α -isomeride, this compound has an agreeable pungent odour of liquorice, which becomes even more intense on boiling the substance with water. A mixture of the two isomerides (α - and β -) in equal proportions melted at 78 — 85° .

*The Isomeric Acetyl-3:4-tolylenediazoimides obtained from
3:4-Tolylenediazoimine.*

3-Nitro-*p*-toluidine when crystallised repeatedly from benzene melted at 117 — 118° (*Ber.*, 1893, **26**, 578; 1897, **30**, 1258). On reduction with tin and hydrochloric acid it yielded 3:4-tolylene-diamine hydrochloride, which was diazotised in a variety of ways with sodium nitrite or methyl nitrite in aqueous and alcoholic solutions. The different preparations of 3:4-tolylenediazoimine (m. p. 83 — 84°) were acetylated with acetic anhydride in water at the ordinary temperature. The products when crystallised from petroleum always gave mixtures of the α - and β -isomerides, which could be separated mechanically. The total crop of crystals from one experiment, when thoroughly powdered, melted at 107 — 115° , and as a mixture of the isomerides in equal proportions melted at 78 — 85° , the higher melting point indicates a preponderance of α -compound in the acetylation product of 3:4-tolylenediazoimine.

Hydrolysis of the Isomeric Acetyl-3:4-tolylenediazoimides.

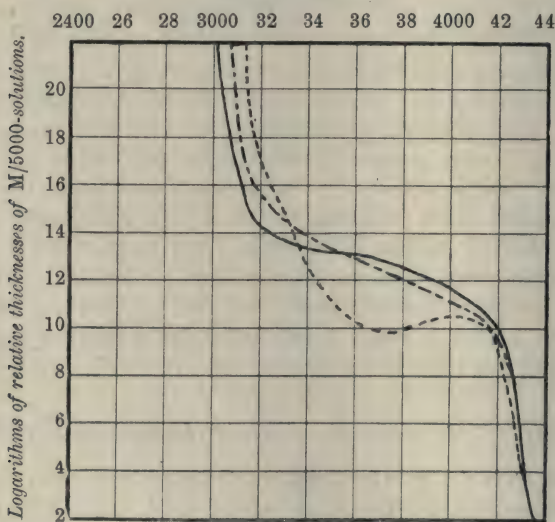
The α -isomeride (m. p. 132°) was hydrolysed by boiling for eight to nine hours with 50 per cent. acetic acid, and the resulting 3:4-tolylenediazoimine again acetylated with acetic anhydride in the presence of water. The product (*A*) melted at 108 — 114° .

The β -isomeride (m. p. 94°) was hydrolysed in the same way, and the resulting diazoimine similarly acetylated. The product (*B*) melted at 110 — 115° . A mixture of *A* and *B* melted at 109 — 115° .

As the pure β -isomeride melts at 93 — 94° the higher melting points of the products *A* and *B* indicate a preponderance in these mixtures of the less fusible α -isomeride.

Absorption Spectra of the α - and β -Isomerides.

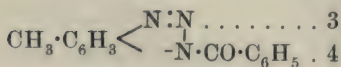
We are indebted to Mr. H. W. Moss for the spectroscopic examination of these isomerides and the mixture of the two obtained by acetylating 3:4-tolylenediazoimine. The solutions were prepared in absolute alcohol, and a Hilger quartz spectrograph was employed with an iron arc as the source of light. The limits of absorption were sharply defined, but, in addition to the absorption shown by the curve, indications were recorded on the plate of a feeble and very shallow absorption band in each of the two isomerides. With the α -compound this weak band lay between $1/\lambda$ 3200 and $1/\lambda$ 3450, and with the β -compound this selective absorption fell between $1/\lambda$ 3400 and $1/\lambda$ 4000. The mixed acetyl compounds from the equilibrium mixture of 3:4-tolylenediazoimine showed the well-defined absorption indicated by the curve, and in addition two feeble, shallow bands corresponding with those of the α - and β -isomerides.

Oscillation frequencies.

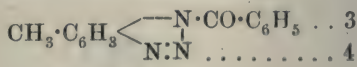
Full curve : α -4-acetyl-3:4-tolylenediazoimide.

Dotted „ : β -3-acetyl-3:4-tolylenediazoimide.

Dot-dash „ : Equilibrium mixture of α - and β -compounds.

II.—The Isomeric Benzoyl-3:4-tolylenediazoimides,

α -M. p. 127–128°.



β -M. p. 122–123°.

4-Benzoyl-3:4-tolylenediazoimide (Formula XXV).

3-Nitrobenzo-*p*-toluidide (formula XXIII), prepared by the Schotten-Baumann reaction from 3-nitro-*p*-toluidine, when crystallised from benzene separated in yellow needles melting at 146—148° (compare *Annalen*, 1881, **208**, 311). This nitro-compound (2 grams), dissolved in alcohol (30 c.c.) and water (10 c.c.) containing ammonium chloride (0.5 gram), was reduced by boiling with excess of zinc dust. 4-Benzoyl-3:4-tolylenediamine (formula XXIV), which separated as a pale yellow precipitate from the filtrate, was recrystallised from alcohol or benzene, and obtained in lustrous, colourless, felted needles, melting at 193—194° (Found, N=12.03. Calc., N=12.38 per cent.). The reduction can be effected, but less satisfactorily with iron filings and dilute acid.

When treated with sodium nitrite in the presence of dilute acetic or hydrochloric acid, 4-benzoyl-3:4-tolylenediamine readily yielded the diazoimide (m. p. 125°), which on crystallisation from light petroleum separated in felted masses of colourless, capillary needles, melting at 127—128°:

0.1722 gave 26.4 c.c. N₂ at 14° and 753 mm. N=17.88.

C₁₄H₁₁ON₃ requires N=17.72 per cent.

4-Benzoyl-3:4-tolylenediazoimide is the sole product of the action of nitrous acid on 4-benzoyl-3:4-tolylenediamine.

4-Nitrobenzo-m-toluidide (Formula XXVI).

The Schotten-Baumann reaction when applied to 4-nitro-*m*-toluidine (m. p. 112°) proceeded less smoothly than in the case of the isomeric 3-nitro-*p*-toluidine. The product separated from petroleum in yellow, prismatic crystals, and from benzene in long, amber-yellow needles, both specimens melting somewhat indefinitely at 83°.

3-Benzoyl-3:4-tolylenediamine (Formula XXVII).

The foregoing compound was reduced with 2 parts of iron filings in 80 parts of water containing acetic acid (1 part). After neutralising with calcium carbonate the solution was filtered hot, and colourless, felted needles of 3-benzoyl-3:4-tolylenediamine separated from the cooled filtrate. Recrystallisation from benzene yielded colourless, felted needles, melting at 158°; from petroleum the base separated in prismatic crystals:

0.1114 gave 11.8 c.c. N₂ at 13° and 754 mm. N=12.41.

C₁₄H₁₄ON₂ requires N=12.38 per cent.

It is noteworthy that the melting point of this compound is not

depressed by admixture with an equal amount of the isomeric 4-benzoyl-3:4-tolylenediamine, the mixed melting point being 180—185°. The two diazoimides derived from these two benzoylated diamines have nearly the same melting points (see above), but the mixed melting point is 102—103°, being about 20° below the melting point of the more fusible isomeride. The anomaly in the mixed melting point of the two benzoyl-3:4-tolylenediamines is probably due to the formation on warming of the far less fusible anhydro-bases, $C_7H_6 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} C \cdot C_6H_5$.

3-Benzoyl-3:4-tolylenediazoimide (Formula XXVIII).

The action of nitrous acid on the preceding compound takes place most smoothly in the absence of mineral acid, and a colourless product is obtainable only when purified 4-benzoyl-3:4-tolylenediamine is employed.

The diamine (1 gram) suspended in water (6 c.c.) was dissolved by adding glacial acetic acid (7 c.c.), and the filtered solution treated with aqueous sodium nitrite in slight excess. The colourless, curdy precipitate (m. p. 116°) when recrystallised from petroleum separated in bulky masses of long, transparent, colourless needles, melting at 122—123°:

0.1888 gave 28.4 c.c. N_2 at 14° and 757 mm. $N = 17.78$.

$C_{14}H_{11}ON_3$ requires $N = 17.72$ per cent.

3-Benzoyl-3:4-tolylenediazoimide is the sole product of the action of nitrous acid on 3-benzoyl-3:4-tolylenediamine.

We desire to express our thanks to the Research Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

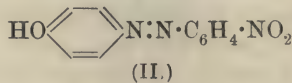
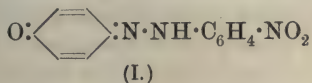
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DUBLIN.

CLII.—*Hydroxyazo-compounds. The Action of Semicarbazide Hydrochloride on the p-Quinones.*

By ISIDOR MORRIS HEILBRON and JAMES ALEXANDER RUSSELL
HENDERSON.

THE investigations which have been carried out in recent years on quinonehydrazones have shown conclusively that these substances are not quinone derivatives, for where such should be

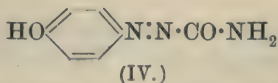
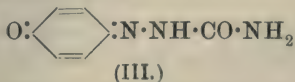
formed rearrangement invariably seems to take place with the formation of the isomeric hydroxyazo-compounds. Thus, Borsche (*Annalen*, 1907, **357**, 171) found that by condensing *o*-nitrophenylhydrazine with *p*-benzoquinone there resulted, not the quinone-hydrazone (I), but the isomeric hydroxyazo-compound (II):



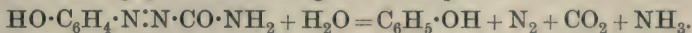
The spectroscopic evidence, at any rate for the *p*-quinone products, supports the view that where hydrazones might be expected, hydroxyazo-compounds are formed. Tuck (T., 1907, **91**, 449) obtained similar absorption curves for benzeneazophenol (quinonehydrazone) and benzeneazophenetole, which latter substance had been proved by Jacobsen and Fischer (*Ber.*, 1892, **25**, 995) to be a typical azo-derivative, and hence was able to show that the parent substance has the same constitution as the ester, that is, it is a true azo-compound.

The present work, a preliminary account of which was recently published (P., 1912, **28**, 256) was undertaken with a view to examine both by chemical and spectroscopic methods the type of compound produced by the action of semicarbazide hydrochloride on the *p*-quinones, and, as might have been expected, owing to the close resemblance in constitution between hydrazine, phenylhydrazine, and semicarbazide, we are able in this paper to show that the condensation products of semicarbazide with the *p*-quinones are not quinonesemicarbazones, but the isomeric hydroxyazo-formamides.

The knowledge of the quinonesemicarbazones previous to the present work was somewhat meagre. Thiele and Barlow (*Annalen*, 1898, **302**, 315) had found that the compound formed by the action of semicarbazide hydrochloride on *p*-benzoquinone in the proportions necessary for the formation of a monosemicarbazone reacted either as a semicarbazone (III) or as 4-hydroxybenzeneazo-formamide (IV):



The evidence in favour of formula III was the production of a disemicarbazone; on the other hand, by boiling the compound with dilute sodium hydroxide, phenol was produced, the decomposition taking place according to the equation:



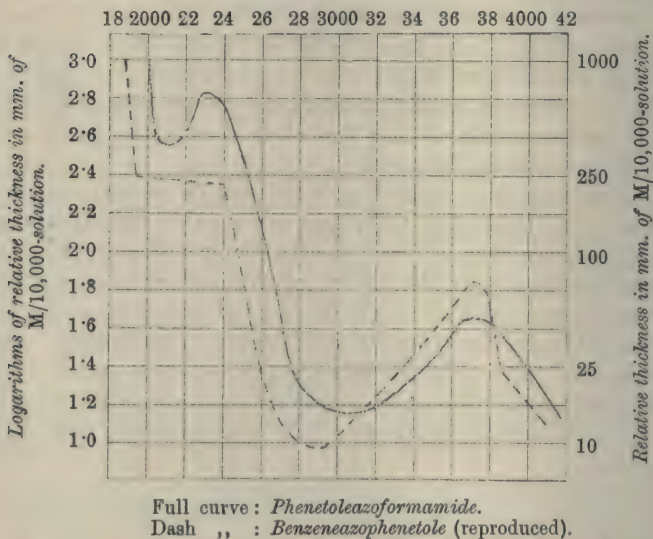
In the light of this reaction Thiele and Barlow conclude that *p*-benzoquinonesemicarbazone is a tautomeric substance, in which

a hydrogen atom wanders from the semicarbazone group to the oxygen atom, thus forming hydroxyl, a change which involves an alteration from a quinonoid to a benzenoid structure.

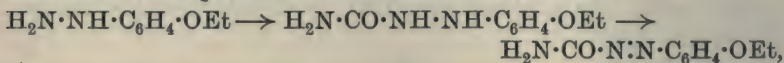
Borsche (*Annalen*, 1904, **334**, 143) reinvestigated the question of tautomerism in some quinonesemicarbazones, but more particularly in the carbamylphenylhydrazone condensation products, and showed that such compounds are apparently tautomeric. The same author also prepared phenetoleazoformamide by the treatment

FIG. 1.

Oscillation frequencies.



of *p*-ethoxyphenylhydrazine with potassium cyanate, followed by oxidation of the product with chromic acid mixture:



a method of preparation proving definitely that the compound is an azo-derivative. The present authors have now prepared this substance directly from benzoquinonesemicarbazone (4-hydroxybenzeneazoformamide), thus obtaining additional proof of the tautomeric change in the parent compound.

Fig. 1 shows the absorption curve of phenetoleazoformamide in alcohol (full curve) and that of benzeneazophenetole (dotted curve), reproduced from Tuck's paper (*loc. cit.*). The absorption curves are very similar, as is to be expected from two compounds of the same type. That these substances are typical azo-derivatives is

further borne out by comparing their absorption curves with that of azobenzene recently described by Crymble, Stewart, and Wright (*Ber.*, 1910, **43**, 1188), which compound shows two bands, one with head at 2200 and the other at 3200, practically identical in position with those of phenetoleazoformamide.

Fig. 2 shows the absorption curves of 4-hydroxybenzeneazo-

FIG. 2.

Oscillation frequencies.

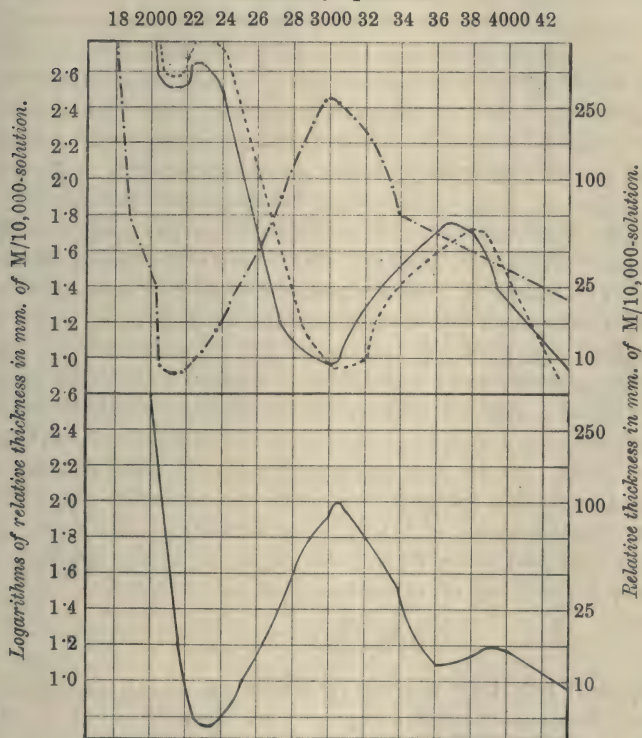


FIG. 3.

FIG. 2. ————— 4-Hydroxybenzeneazoformamide.
 - - - - - Acetyl derivative. + NaOEt.
 Acetyl derivative.

FIG. 3. Tetraphenylquinodimethane.

formamide in alcohol (full curve) and of its acetyl derivative (dotted curve), both of which are identical with the azo-compound, phenetoleazoformamide; hence it is clear, at any rate under the conditions of examination, that *p*-benzoquinonesemicarbazone only exists in its isomeric form as a typical azo-derivative.

The addition of sodium ethoxide to 4-hydroxybenzeneazoformamide causes a complete change in the absorption spectrum, as is shown in Fig. 2 (dot-dash curve). This change in the type of absorption on the addition of sodium ethoxide is common to all the substances examined, as a glance at Figs. 4, 5, 6, and 7 will serve to show.

We have thus direct evidence that the salts of the hydroxyazoformamides are not azo-derivatives, but undoubtedly possess some other structure. A somewhat similar change in absorption on salt formation has been found to occur with *p*-nitrophenol (Baly, Edwards, and Stewart, T., 1906, **89**, 514), the salt of this compound showing an absorption band closely resembling those of the salts of the hydroxyazoformamides. According to these authors, the salts of *p*-nitrophenol are quinonoid, and although in a more recent paper Baly, Tuck, and Marsden (T., 1910, **97**, 571) have rejected this view, other investigators still hold to the quinonoid structure of the nitrophenol salts (compare Hewitt, Pope, and Willett, T., 1912, **101**, 1770; Hantzsch, *Ber.*, 1913, **46**, 1537); hence it may be possible that the salts of the series under investigation are also quinonoid in structure. In order to determine this point, it appeared to us necessary to examine spectrographically some substance possessing undoubted quinonoid structure, as a type of quinone more definite than *p*-benzoquinone (which compound possesses characteristic ketonic properties), and one in which, as in the quinonoid salts in question, the simple isorropic vibration assumed by Baly and Stewart (T., 1906, **89**, 502) to be the cause of colour, was excluded. With this end in view we obtained from Prof. Staudinger, to whom our best thanks are due, a specimen of tetraphenylquinodimethane,



a compound fulfilling the above conditions in all essentials. The absorption curve of this compound in either alcohol or ether is shown in Fig. 3, and, as will be seen, it possesses a characteristic band of considerable persistence with head at about 2300 and a small band in the ultra-violet with head at about 3600 in *M*/10,000-solution, the selective absorption being very similar to that of the hydroxybenzeneazoformamide salts and also to the quinonehydrazone salts obtained by Tuck (*loc. cit.*).

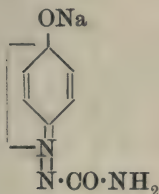
It follows, therefore, that a further change in constitution takes place in the *p*-benzoquinone condensation products on salt formation, for whereas the free substances as examined in solution are typical azo-compounds, the salts are quinonoid in structure.

The same will then apply to the salts of the nitrophenols, the

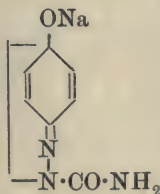
absorption spectra of which are so similar to that of the typical quinone (tetraphenylquinodimethane) represented in Fig. 3, and thus the principal objection to a quinonoid structure for the salts of the nitrophenols brought forward by Baly, Tuck, and Marsden, namely, that the characteristic band of the salts appeared at a different dilution from that of the quinones cannot be upheld. We suggest, indeed, as a result of this examination of tetraphenylquinodimethane, that the band of benzoquinone and its homologues appearing in $M/10$ -solution is directly due to the diketo-group, such as is present in diacetyl, as this substance gives a similar band to that of p -benzoquinone and its homologues.

The exact constitution of the salts has not at present been successfully elucidated, but we suggest, in the meantime, that either formula V or VI may possibly represent a structure in harmony with the experimental evidence, obtained from the study of the absorption spectra of these compounds.

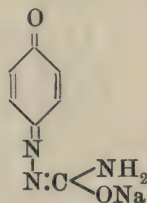
Formula VII, which represents a true quinonoid structure for the salts of hydroxyazoformamides, has also been considered, but is unacceptable for two reasons. In the first place, such a formula is precluded in the similarly constituted salts of the quinone-hydrazones obtained by Tuck (*loc. cit.*), and secondly, with simple semicarbazones, no change in absorption takes place on addition of alkali, as would be expected to occur, if salt formation was produced:



(V.)



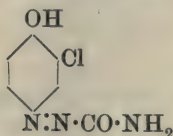
(VI.)



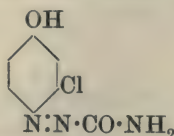
(VII.)

Monochloro-p-benzoquinone and Semicarbazide Hydrochloride.

Theoretically, two isomeric hydroxyazo-compounds are possible in this case, as indicated by the formulæ VII and VIII:



(VII.)



(VIII.)

but only one could be isolated, namely, that represented by formula VII, as is proved by the formation of o -chlorophenol on

heating with dilute sodium hydroxide. The condensation product in this case reacts only as an azo-compound, no disemicarbazone being formed.

2 : 6-Dichloro-p-benzoquinone.—The hydroxyazo-compound formed

FIG. 4.

Oscillation frequencies.

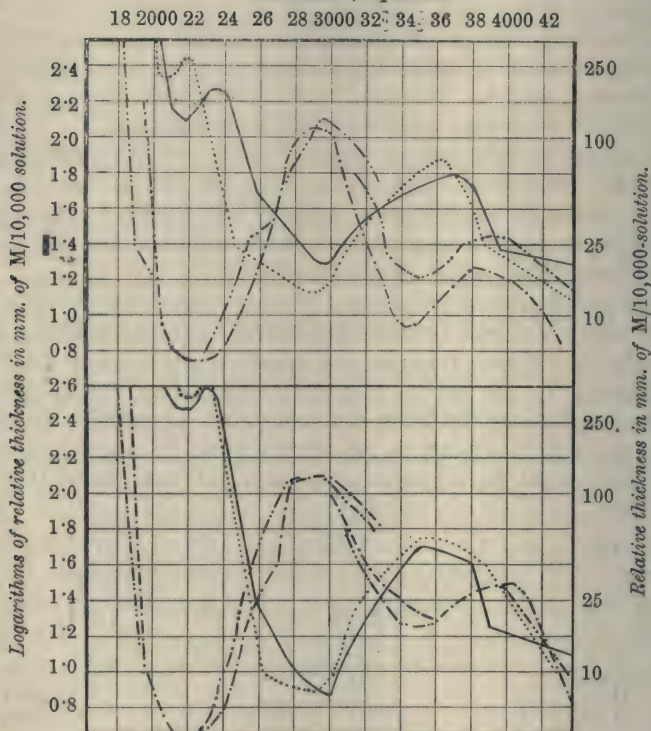


FIG. 5.

FIG. 4. ————— 3-Chloro-4-hydroxybenzeneazofornamide.
 - - - - - " " " " + NaOEt.
 3:5-Dichloro-4-hydroxybenzeneazofornamide.
 - · - · - · " " " " + NaOEt.

FIG. 5. ————— 4-Hydroxy-m-tolueneazofornamide.
 - - - - - " " " " + NaOEt.
 4-Hydroxy-3-methyl-5-isopropylbenzeneazofornamide.
 - · - · - · " " " " + NaOEt.

here is 3:5-dichloro-4-hydroxybenzeneazofornamide, as is proved by the production of 2:6-dichlorophenol on treatment with dilute sodium hydroxide. Neither the isomeric 1:6-dichloro-4-hydroxybenzeneazofornamide nor a disemicarbazone could be obtained.

Fig. 4 represents the absorption curves of the above compounds,

the parent substances in each case being typical azo-derivatives, the salts, on the other hand, showing the characteristic quinonoid graphs.

Toluquinone.—The condensation product in this case is 4-hydroxy-*m*-tolueneazoformamide; one only of the two theoretically possible isomerides was obtained. Proof of this constitution is afforded by the production of *o*-cresol on treatment with alkali. As in the case of the benzoquinone mono-condensation product, 4-hydroxy-*m*-tolueneazoformamide can act tautomerically, a disemicarbazone being obtainable, although in solution, as shown spectrographically in Fig. 5, this compound, like 4-hydroxybenzeneazoformamide itself, exists only as an azo-derivative.

Thymoquinone.—The condensation product was 4-hydroxy-3-methyl-5-isopropylbenzeneazoformamide, yielding thymol with warm sodium hydroxide solution. The compound is a typical azo-derivative, as shown in Fig. 5, and reacts only as such.

Bromination Products of the Hydroxybenzeneazoformamides.

Such compounds are readily obtained by direct action of bromine on the hydroxyazoformamides themselves, mono- and di-bromo-derivatives in several cases being isolated. These bromo-substitution products are typical hydroxyazo-compounds, as is shown by the graphs in Figs. 6 and 7.

In the case of toluquinone and of these chlorinated benzoquinones (which react with semicarbazide), only one of the two theoretically possible isomerides could be isolated, and in each case the azoformamide group is attached to the benzene nucleus remote from the substituents. With thymoquinone the azoformamide group is adjacent to the methyl in preference to the *isopropyl* radicle.

Further, although *p*-benzoquinone and toluquinone form disemicarbazones, monochloro-*p*-benzoquinone, 2:6-dichloro-*p*-benzoquinone and thymoquinone react with only one molecule of semicarbazide, the product formed being essentially an azo-derivative, whilst with 2:5-dichloro-*p*-benzoquinone, trichloro-*p*-benzoquinone, chloroanilic acid, and dibromothymoquinone no reaction took place.

Kehrmann (*Ber.*, 1888, **21**, 3315) found a similar phenomenon when studying the action of hydroxylamine on the substituted quinones, and Staudinger (*Ber.*, 1908, **41**, 1355) observed something similar in studying the action of diphenylketene on the substituted quinones. Whether this inactivity is due to steric hindrance or some other cause remains at present indefinite, but it is evidently general for a large series of various condensation products, further evidence of which is shown in the present case.

Colour Isomerism.—In two cases, namely, with *p*-benzoquinone and 2:6-dichloro-*p*-benzoquinone, red modifications of the condensation product were obtained in addition to the yellow forms. The cause of this difference cannot at present be definitely decided,

FIG. 6.

Oscillation frequencies.

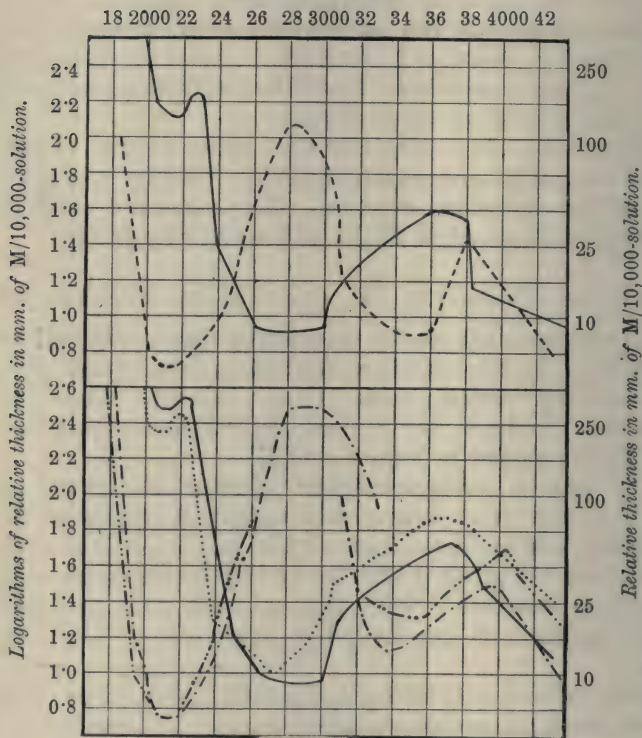


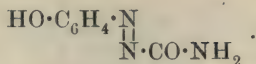
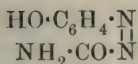
FIG. 7.

FIG. 6. ————— 5-Bromo-4-hydroxy-m-tolueneazoforamamide.
 - - - - - " " " + NaOEt.

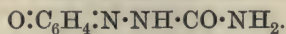
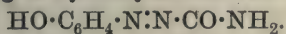
FIG. 7. ————— 3-Bromo-4-hydroxy-2-methyl-5-isopropylbenzeneazoforamamide.
 - - - - - " " " + NaOEt.
 Dibromo-derivative of 4-hydroxy-2-methyl-5-isopropylbenzeneazoforamamide.
 - " " " + NaOEt.

but the following possibilities are put forward as probable explanations.

1. The difference in colour may be due to stereoisomerism, in which the two forms may be *syn*- and *anti*-compounds:



2. The difference may be due to structural change, one form being a hydroxyazo-derivative and the other a semicarbazone:



3. The colour difference may be due to valency isomerism in accordance with Hantzsch's views.

4. The difference of colour may be due to dimorphism.

In solution both modifications are identical and exhibit the characteristic absorption of azo-compounds.

The Relation between Molecular Weight and Position of Absorption Band.

In the following table the hydroxyazoformamides are arranged according to their molecular weights, the third column denoting the position of the head of the principal band, and showing that increase in molecular weight tends to push the band towards the red end of the spectrum:

Compound.	Molecular weight.	Head of band.	λ .	Difference from mean value 2174
$\text{C}_7\text{H}_7\text{O}_2\text{N}_3$	165	3000	2165	-9
$\text{C}_8\text{H}_9\text{O}_2\text{N}_3$	179	3000	2179	5
$\text{C}_9\text{H}_{11}\text{O}_2\text{N}_3$	193	3000	2193	19
$\text{C}_7\text{H}_6\text{O}_2\text{N}_3\text{Cl}$	199.5	2950	2167	-7
$\text{C}_9\text{H}_9\text{O}_3\text{N}_3$	207	2950	2174	0
$\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}_3$	221	2900	2154	-20
$\text{C}_7\text{H}_5\text{O}_2\text{N}_3\text{Cl}_2$	234	2900	2167	-7
$\text{C}_8\text{H}_6\text{O}_2\text{N}_3\text{Br}$	258	2900	2191	17
$\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}_3\text{Br}$	300	2800	2167	-7
$\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}_3\text{Br}_2$	379	2700	2179	5
Mean			2174	

FIG. 8.

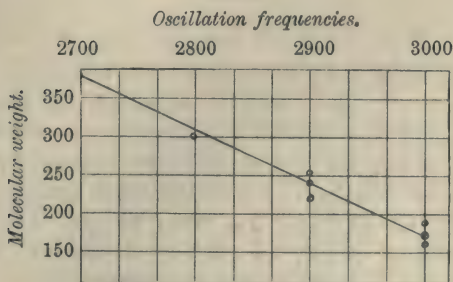


Fig. 8 shows that the graph obtained by taking the heads of the bands as abscissæ and the molecular weights as ordinates is, allowing for possible slight experimental errors, a straight line.

In the simple equation $y = mx + k$, if for y we substitute M , the molecular weight, and $1/\lambda$ (head of band) for x , this becomes $M = m/\lambda + k$, whence, by substituting numerical values for M and $1/\lambda$, $m = -\frac{2}{3}$, and $k = \frac{2}{3}1/\lambda + M = 2174$ (the mean value).

A close relationship thus evidently exists between the molecular weight and the head of the band in this series of similarly constituted compounds, and doubtless the same holds for other series.

EXPERIMENTAL.

4-Hydroxybenzeneazoformamide (p-Benzoquinonesemicarbazone).

This compound was prepared by Thiele and Barlow (*Annalen*, 1898, **302**, 315), who, by acting on a boiling solution of *p*-benzoquinone in alcohol with aqueous semicarbazide hydrochloride, obtained a mixture of the mono- and the di-semicarbazone. Borsche (*Annalen*, 1904, **334**, 175), by working at room temperature, obtained only the mono-derivative. On repeating the preparation as described by Borsche, small quantities of the disemicarbazone were invariably obtained, but on carrying out the operation in ice-cold solutions the formation of the disemicarbazone was wholly avoided.

The colour of the product obtained, even under apparently identical conditions, was found to vary considerably. Sometimes the compound was precipitated in yellow crystals, and at other times a mixture of the yellow with a red variety was obtained.

Yellow Modification.—This is readily obtained pure by dissolving either form in acetone and precipitating by means of light petroleum or carbon disulphide. It may also be prepared from the red modification by rapid crystallisation from hot water. It is thus obtained in tiny yellow needles, melting and decomposing at 165—166°:

0.1506 gave 31.9 c.c. N_2 at 12° and 765 mm. $N = 25.31$.

$C_7H_7O_2N_3$ requires $N = 25.45$ per cent.

Red Modification.—This form is obtained by allowing a hot aqueous solution of the yellow modification to cool slowly or by precipitation of a hot acetone solution by hot benzene. It forms small, red needles, having the same melting point as the yellow isomeride. The change from one form to the other must take place at the melting point, as prolonged heating, even at temperatures near the melting point, causes no change in colour of either form:

0.1580 gave 33.5 c.c. N_2 at 12° and 765 mm. $N = 25.33$.

$C_7H_7O_2N_3$ requires $N = 25.45$ per cent.

Both modifications are equally soluble in water, alcohol, acetone, or glacial acetic acid, giving orange-coloured solutions, and when boiled with dilute sodium hydroxide, yield phenol.

Sodium Salt of 4-Hydroxybenzeneazoformamide,
 $\text{NaO} \cdot \text{C}_6\text{H}_4 \cdot \text{N}:\text{N} \cdot \text{CO} \cdot \text{NH}_2$.

This salt is readily prepared by dissolving the parent compound in acetone, adding sodium ethoxide solution in slight excess, and precipitating by means of light petroleum. The salt is purified by dissolving in acetone, filtering off any excess of sodium ethoxide, and reprecipitating with light petroleum. In this way it is obtained in small, red crystals, soluble in water, alcohol, or acetone:

0.3472 gave 0.1304 Na_2SO_4 . $\text{Na} = 12.16$.

$\text{C}_7\text{H}_6\text{O}_2\text{N}_3\text{Na}$ requires $\text{Na} = 12.39$ per cent.

The *silver* salt is obtained as a ruby-red powder by precipitating an aqueous solution of the sodium salt with silver nitrate.

Phenetoleazoformamide, $\text{EtO} \cdot \text{C}_6\text{H}_4 \cdot \text{N}:\text{N} \cdot \text{CO} \cdot \text{NH}_2$.

This compound was prepared indirectly by Borsche as described on p. 1406. It has now been prepared directly by heating an acetone solution of 4-hydroxybenzeneazoformamide for several hours on a water-bath under a reflux condenser, with the necessary quantities of dry silver oxide and ethyl iodide. After removing the silver iodide by filtration and distilling off the acetone, the solid residue of the ethyl ether was repeatedly crystallised from methyl alcohol. It is obtained in orange-red leaflets, melting at 162° , soluble in water, alcohol, or acetone, but insoluble in chloroform, or benzene (Found, $\text{N} = 21.89$. $\text{C}_9\text{H}_{11}\text{O}_2\text{N}_3$ requires $\text{N} = 21.76$ per cent.).

4-Acetoxybenzeneazoformamide, $\text{AcO} \cdot \text{C}_6\text{H}_4 \cdot \text{N}:\text{N} \cdot \text{CO} \cdot \text{NH}_2$.

To a solution of 4-hydroxybenzeneazoformamide in absolute alcohol the necessary quantities of sodium, dissolved in alcohol, and acetyl chloride were added. After allowing the mixture to remain for about an hour, the precipitated sodium chloride was removed, and the filtrate allowed to evaporate. From the residue, on crystallisation from alcohol, the acetyl derivative was obtained in long, orange-red needles, melting and decomposing at 158° :

0.1496 gave 26.8 c.c. N_2 at 20° and 756 mm. $\text{N} = 20.38$.

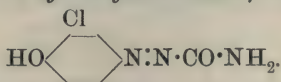
$\text{C}_9\text{H}_9\text{O}_3\text{N}_3$ requires $\text{N} = 20.29$ per cent.

Bromination of 4-Hydroxybenzeneazoformamide: 3:5-Dibromo-4-hydroxybenzeneazoformamide.

This compound was prepared as described by Borsche (*Annalen*, 1904, **334**, 175); it forms yellow needles, melting and decomposing at 223—225°.

The *sodium* salt is obtained in small, red needles by the method already described.

3-Chloro-4-hydroxybenzeneazoformamide,



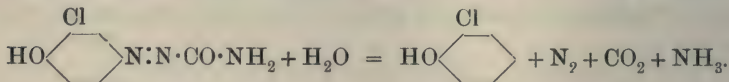
Seven grams of monochloro-*p*-benzoquinone, prepared according to Levy and Schultz's method (*Annalen*, 1881, **210**, 138, 145), were dissolved in ice-cold alcohol, and mixed with an aqueous solution of 5.5 grams of semicarbazide hydrochloride. The yellowish-brown product which separated was collected, washed with water, and crystallised from acetone with the addition of light petroleum.

The compound is thus obtained in deep yellow crystals, melting and decomposing at 185°. It is soluble in water, alcohol, or acetone, but insoluble in chloroform or benzene:

0.1518 gave 27.4 c.c. N₂ at 17° and 760 mm. N = 20.96.

C₇H₆O₂N₃Cl requires N = 21.05 per cent.

On boiling 3-chloro-4-hydroxybenzeneazoformamide with dilute sodium hydroxide, there is obtained *o*-chlorophenol (b. p. 175°). The decomposition may be represented by the following equation:



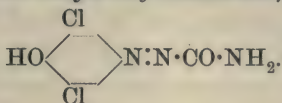
From the formation of *o*-chlorophenol it is evident that the semicarbazide attacks the oxygen atom remote from the chlorine.

The *sodium* salt forms dark red crystals:

0.2734 gave 0.0865 Na₂SO₄. Na = 10.25.

C₇H₅O₂N₃ClNa requires Na = 10.38 per cent.

Attempts to prepare a disemicarbazone from chloro-*p*-benzoquinone were unsuccessful.

3:5-Dichloro-4-hydroxybenzeneazoformamide,

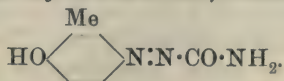
8·8 Grams of 2:6-dichloro-*p*-benzoquinone were dissolved in 200 c.c. of alcohol, and to the well-cooled solution a cold solution of 8·5 grams of semicarbazide hydrochloride in 30 c.c. of water was added. After allowing the mixture to remain in the ice-chest overnight, the orange-red precipitate formed was collected and washed with water. On examining the product with a lens, it was seen to consist of a mixture of red and yellow needles, with the red predominating. The substance was purified by precipitating the acetone solution with light petroleum, when it was obtained in minute, yellow needles, melting and decomposing at 218°:

0·1508 gave 22·5 c.c. N_2 at 15° and 761 mm. $\text{N}=17\cdot79$.

$\text{C}_7\text{H}_5\text{O}_2\text{N}_3\text{Cl}_2$ requires $\text{N}=17\cdot95$ per cent.

Red Modification.—In attempting to prepare a disemicarbazone of 2:6-dichloro-*p*-benzoquinone by the action of excess of semicarbazide hydrochloride, a red precipitate, melting and decomposing at 218°, was formed, which proved to be the isomeric modification of 3:5-dichloro-4-hydroxybenzeneazoformamide, and not a disemicarbazone. Attempts to recrystallise this red isomeride as such proved fruitless, the yellow variety being invariably obtained.

Attempts to prepare condensation products of semicarbazide with 2:5-dichloro-*p*-benzoquinone, trichloro-*p*-benzoquinone, tetrachloro-*p*-benzoquinone, and chloroanilic acid were all unsuccessful.

4-Hydroxy-m-tolueneazoformamide,

This compound was prepared from toluquinone by a method quite similar to that used in the previous preparations. It crystallises from hot alcohol in yellow needles, melting at 178—179°:

0·155 gave 31·1 c.c. N_2 at 16° and 759 mm. $\text{N}=23\cdot38$.

$\text{C}_8\text{H}_9\text{O}_2\text{N}_3$ requires $\text{N}=23\cdot46$ per cent.

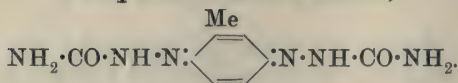
When boiled with dilute sodium hydroxide, the compound yields *o*-cresol, a reaction which proves that it is the oxygen atom remote from the methyl group that reacts with the semicarbazide base.

The *sodium* salt forms dark red crystals:

0.3521 gave 0.1227 Na_2SO_4 . $\text{Na}=11.28$.

$\text{C}_8\text{H}_8\text{O}_2\text{N}_3\text{Na}$ requires $\text{Na}=11.44$ per cent.

Toluquinonedisemicarbazone,



Two grams of 4-hydroxy-*m*-tolueneazoformamide were dissolved in alcohol, and to the boiling solution an aqueous solution of 1.2 grams of semicarbazide hydrochloride was added, and the mixture heated on the water-bath for an hour. On keeping, an orange-red precipitate separated out; this was collected, washed with water, and dried. The disemicarbazone obtained in this way melts and decomposes at 240° :

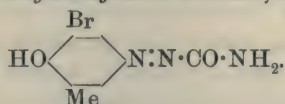
0.1218 gave 36.5 c.c. N_2 at 13° and 760 mm. $\text{N}=35.42$.

$\text{C}_9\text{H}_{12}\text{O}_2\text{N}_6$ requires $\text{N}=35.59$ per cent.

It is evident from the formation of a disemicarbazone in this way that 4-hydroxy-*m*-tolueneazoformamide acts, like 4-hydroxybenzeneazoformamide, tautomerically, differing in this respect from 3-chloro-4-hydroxybenzeneazoformamide, where the presence of the acidic chlorine atom apparently only allows of the azo-structure.

Bromine Derivatives of 4-Hydroxy-m-tolueneazoformamide:

5-Bromo-4-hydroxy-m-tolueneazoformamide,



Four grams of 4-hydroxy-*m*-tolueneazoformamide, dissolved in 100 c.c. of glacial acetic acid, were mixed with 12 grams of sodium acetate, and a solution of 1 c.c. of bromine in 50 c.c. of glacial acetic acid slowly added. After an hour the mixture was treated with a little water; a yellow precipitate separated, and this was collected and washed with water and alcohol. After repeated crystallisations from boiling alcohol, the monobromo-compound was obtained in yellow needles, melting and decomposing at 205° . It is soluble in water, alcohol, or acetone, but insoluble in benzene, ether, or chloroform; it dissolves in sodium hydroxide solution, yielding a deep red solution of the sodium salt:

0.1394 gave 20 c.c. N_2 at 19° and 755 mm. $\text{N}=16.39$.

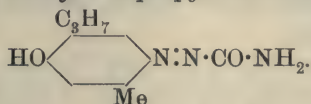
$\text{C}_8\text{H}_8\text{O}_2\text{N}_3\text{Br}$ requires $\text{N}=16.28$ per cent.

The exact position of the bromine atom in the ring is uncertain,

but by comparison with the analogous compound of known composition obtained by Borsche (*loc. cit.*) on brominating 4-hydroxy-*m*-tolueneazoformanilide, it may be assumed that here also the bromine atom enters the ring in the ortho-position with respect to the hydroxyl group.

Attempts to prepare a pure dibromo-derivative of 4-hydroxy-*m*-tolueneazoformamide were unsuccessful, resulting, as deduced from melting-point determinations and analyses, in mixtures of the monobromo- with higher bromo-derivatives exceedingly difficult to separate. Unfortunately, the quantity of material in our hands did not allow of further investigation.

4-Hydroxy-2-methyl-5-isopropylbenzeneazoformamide,



Eight grams of thymoquinone were dissolved in alcohol, and to the well-cooled solution a cold aqueous solution of 4 grams of semicarbazide hydrochloride was added. After the mixture had remained for some hours in the ice-chest, the yellow precipitate which formed was collected, washed, dried, and crystallised from alcohol. It is thus obtained in bright yellow needles, melting and decomposing at 201—202°:

0.1504 gave 25 c.c. N_2 at 18° and 754 mm. $N=19.04$.

$C_{11}H_{15}O_2N_3$ requires $N=19.0$ per cent.

The sodium salt was obtained in large ruby-red crystals:

0.3552 gave 0.1052 Na_2SO_4 . $Na=9.59$.

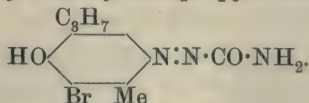
$C_{11}H_{14}O_2N_3Na$ requires $Na=9.46$ per cent.

When boiled with dilute sodium hydroxide solution, the compound is completely decomposed with production of thymol, a reaction which indicates its structure.

No disemicarbazone could be obtained from thymoquinone.

Bromination of 4-Hydroxy-2-methyl-5-isopropylbenzeneazoformamide.

3-Bromo-4-hydroxy-2-methyl-5-isopropylbenzeneazoformamide,



This compound was prepared by a method similar to that used in the case of 5-bromo-4-hydroxy-*m*-tolueneazoformamide. After

crystallisation from alcohol, it is obtained in yellow needles, melting and decomposing at 218° . It is soluble in water, alcohol, or acetone, but insoluble in benzene or chloroform:

0.1637 gave 20.4 c.c. N_2 at 21° and 754 mm. $N=14.07$.

$C_{11}H_{14}O_2N_3Br$ requires $N=14.0$ per cent.

Preparation of a Dibromo-derivative of 4-Hydroxy-2-methyl-5-isopropylbenzeneazoformamide.

This compound was obtained by acting on the parent substance dissolved in glacial acetic acid with excess of bromine in the presence of sodium acetate. After several recrystallisations from alcohol, it was obtained in small, yellow needles, melting and decomposing at 245° ; it is soluble in water, alcohol, or acetone, but insoluble in benzene or chloroform:

0.1846 gave 18.4 c.c. N_2 at 18° and 744 mm. $N=11.26$.

$C_{11}H_{13}O_2N_3Br_2$ requires $N=11.08$ per cent.

In order to elucidate the position of the second bromine atom in the compound, an attempt was made to prepare a hydroxyazo-derivative of dibromothymoquinone, but proved unsuccessful, no reaction taking place. This fact makes it doubtful whether the second bromine atom enters the nucleus or displaces hydrogen in the side-chain.

Attempt to Prepare a Semicarbazone of p-Benzoquinonechloroimide.

As the compounds formed by the action of semicarbazide hydrochloride on *p*-benzoquinone and its derivatives in the proportions necessary for the formation of monosemicarbazones were found to be undoubted azo-compounds, it was considered advisable to attempt to prepare a compound in which a change from a semicarbazone to the isomeric hydroxyazo-structure was excluded. With this end in view, an attempt was made to prepare a semicarbazone of *p*-benzoquinonechloroimide.* By acting on *p*-benzoquinonechloroimide in the usual manner with semicarbazide hydrochloride, a yellow precipitate, evidently of the desired semicarbazone, was immediately formed, but, despite every precaution, decomposed before it could be collected.

Summary.

1. The compounds formed by the interaction of equimolecular proportions of the *p*-quinones and semicarbazide hydrochloride are

* *p*-Benzoquinoneoximesemicarbazone would be suitable, but as Thiele and Barlow (*loc. cit.*) have pointed out that it is insoluble in alcohol or water, it would be impossible to study its absorption spectrum.

not semicarbazones, but hydroxyazo-derivatives. This is proved by their absorption spectra being of the type of those of azobenzene and other typical azo-compounds.

2. Quinonesemicarbazones must, however, in some of the compounds be formed under certain conditions, as is shown by the formation of disemicarbazones.

3. The salts of the hydroxybenzeneazoformamides, on the other hand, possess quinonoid structure, as is proved by their absorption curves being of the same type as that of the undoubted quinonoid compound, tetraphenylquinodimethane.

4. The position isomerides, theoretically possible, cannot be obtained, owing to what is generally accepted as steric hindrance.

5. A direct relationship exists between the molecular weight and positions of the absorption bands in this series of similarly constituted compounds.

In conclusion, we desire to take this opportunity of expressing our indebtedness to Prof. Henderson for the interest he has taken in this work.

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CLIII.—*The Relative Activities of Certain Organic Iodo-compounds with Sodium Phenoxide in Alcoholic Solution. Part II. iso-, sec., and tert.-Alkyl Iodides.*

By DAVID SEGALLER.

IN a former paper (this vol., p. 1154) the author gave an account of the relative activities of the normal primary alkyl iodides as measured by the velocities of their reaction with sodium phenoxide in alcoholic solution with the formation of phenyl alkyl ethers. The first eight homologues and cetyl iodide were considered, and it was shown that there is a regular decrease in activity with increase in the weight of the molecule, the one exception being amyl iodide, which was by far the least reactive of the series. It was also shown that the initial concentration had a profound influence on the value of the velocity-coefficient, so that comparable results can be obtained only by using solutions of the same initial concentrations. This part of the investigation deals with *isopropyl*, *isobutyl*,

*iso*amyl, *sec.*-butyl, *sec.*-amyl, *sec.*-hexyl, *sec.*-heptyl, *sec.*-octyl, *tert.*-butyl, *tert.*-amyl, and allyl iodides. Although not an alkyl iodide, allyl iodide was included on account of its general interest and to give an indication of the effect of unsaturation. Very few of the above-mentioned substances have been dealt with by other investigators from a dynamic point of view, and (with the exception of *isopropyl* and *isobutyl iodides*) none of them at all extensively. Menschutkin (*Zeitsch. physikal. Chem.*, 1890, **5**, 589), in measuring the "affinity-coefficients of the aliphatic alkyl iodides" with triethylamine in acetone solution, dealt also with *isobutyl* iodide and with *isopropyl* iodide, and found that in both cases the normal primary compound was more reactive than the *iso*-compound, *n*-propyl iodide being nearly ten times as reactive as *isopropyl* iodide, and *n*-butyl iodide about four times as active as *isobutyl* iodide.

He was not able to measure the velocity of tertiary iodides, since these do not react with triethylamine to form ammonium compounds, and in certain cases are decomposed by it, with the formation of olefines.

Wislicenus (*Annalen*, 1882, **212**, 239) investigated the times required for complete reaction between alkyl iodides and ethyl sodioacetate. He found *isobutyl* iodide only half as reactive as *isopropyl* iodide, whereas in the case of *tert.*-butyl iodide there was no formation of ψ -butylacetic ether. On the other hand, allyl iodide by this method was found to be extremely reactive.

Wildermann (*Zeitsch. physikal. Chem.*, 1891, **7**, 661) studied the velocity of reaction of alcoholic potassium on the halogen derivatives of the fatty hydrocarbons, and found *iso*amyl iodide less reactive than *isopropyl* iodide, and this less reactive than *sec.*-hexyl iodide.

The same reaction was investigated by Brusoff (*Zeitsch. physikal. Chem.*, 1900, **34**, 129) from a different point of view. This investigator determined the volume of olefine obtained at the temperature of the boiling point of benzene when an alkyl iodide is heated with alcoholic potassium hydroxide. He took such quantities of each reacting substance that the maximum volume of olefine obtainable was 300 c.c.

He also measured the maximum velocity of each reaction, since, owing to the increase in temperature of the mixture from that of the room to that of the surrounding boiling benzene, the velocity rose to a maximum, and then was fairly steady. Brusoff investigated only those alkyl iodides which yielded gaseous olefines, and the following figures give the maximum relative velocities found by him in this way.

Propyl iodide.....	1.12	<i>iso</i> Butyl iodide	1.42
<i>iso</i> Propyl iodide	1.42	<i>sec.</i> -Butyl „	2.53
Butyl „	0.50	<i>tert.</i> -Butyl „	4.00

From these experiments Brussoff concludes that:

(a) The smallest amount of olefine is yielded by the normal primary chain, the amount of ether formed being the largest. In the case of *isobutyl* iodide the large yield of olefine cannot be looked for in the position of the iodine atom, which is situated in the primary alcohol group, but is to be explained by the structure of the chain.

In *isobutyl* iodide, among the primary alkyl iodides, the conditions are most favourable for the elimination of hydrogen iodide, since the side-chain is attached nearest to the carbon atom to which the iodine is bound. It is to be assumed from the work of Menschutkin that when the side-chain in the primary iodides becomes removed from the iodine atom that the formation of olefine will be less.

(b) The secondary iodides yield no ether with alcoholic potassium hydroxide, the reaction going to produce olefine entirely. The reason here again is one of structure, the side-chain being attached to the carbon atom to which the iodine atom is bound, and therefore the secondary iodides are most suited for the formation of olefine.

(c) With tertiary iodides there is some formation of ether, and therefore less olefine.

The results of the experiments described in the present paper show that no such general conclusions as those of Brussoff can be drawn. The reactivity of the alkyl iodides depends, not only on their structure, but very much more so on the reagent with which their reaction-velocities are measured.

Different investigators have found different relative reactivities for these compounds, and a wide disagreement is found if one attempts to interpret the results of these researches. Burke and Donnan (T., 1904, **85**, 555), for example, find *isopropyl* iodide about 200 times as reactive as *isobutyl* iodide, whereas Preston and Jones (T., 1912, **101**, 1930) find allyl iodide much faster than methyl iodide when its reaction-velocity is measured with dimethyl-aniline, but slower than methyl iodide towards tri*iso*amylamine.

The following table summaries the results obtained by other investigators. For the object of comparison, *n*-propyl iodide has been taken as the standard.

Relative Velocity-coefficients.

	Wislicenus.	Men- schutkin.	Wilderman.	Brussoff.	Burke and Donnan.
<i>n</i> -Propyl.....	1.0	1.0	1.0	1.0	1.0
<i>iso</i> Propyl	0.34	0.1	0.7	1.27	22.0
<i>iso</i> Butyl.....	0.16	0.1	—	1.27	0.14
<i>sec.</i> -Butyl	—	—	—	2.26	—
<i>tert.</i> -Butyl	—	—	—	3.57	—
<i>iso</i> Amyl	—	—	0.4—1.5	—	0.57
<i>sec.</i> -Hexyl	—	—	2.4—3.2	—	—

EXPERIMENTAL.

The method used for measuring the velocity-coefficients has been described in the communication dealing with the normal primary alkyl iodides (*loc. cit.*), and the same procedure was adopted in the following experiments with some necessary modifications. With those substances very sensitive to the action of light, for example, *isopropyl* iodide, *tert.*-butyl iodide, and allyl iodide, every precaution was taken to exclude light as much as possible by using pipettes which had been silvered on the outside. The method adopted with the tertiary iodides was different from that in all the other cases, for, as is well known, these compounds are rapidly decomposed by water, even in the cold.

The acid used in this case was a *N*/100-solution of dry hydrogen chloride in absolute ethyl alcohol. To stop the reaction the contents of the tube were emptied into a vessel containing this alcoholic acid solution kept cold by a surrounding freezing mixture. The titration was then completed from a burette. The indicator used was an alcoholic solution of lacmoid, since phenolphthalein is quite unsuitable in the presence of quantities of alcohol, whereas lacmoid gives very constant results in such circumstances.

For the reason explained above, all solutions (with exception of allyl iodide) were *N*. The measurements were carried out at 42.5° as before, and the preparations of the iodides were in all cases but one those of Kahlbaum.

isoButyl Iodide.

Each mixture contained 5 c.c. of *N*-isobutyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = *N*/5; γ = 25.00.

I.

Zero = 24.38 c.c.

<i>t.</i>	<i>a - x.</i>	<i>x.</i>	<i>k.</i>
120	22.59	1.79	0.0006603
250	21.02	3.36	0.0006399
420	19.10	5.28	0.0006596
480	18.60	5.78	0.0006477
540	18.10	6.28	0.0006430
800	16.03	8.35	0.0006500

$$k \text{ mean} = 0.0006501$$

$$K = k \times 25/24.38 = 0.0006665$$

II.

$$K \text{ mean} = 0.0006590$$

isoAmyl Iodide.

Each mixture contained 5 c.c. of *N*-isoamyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = $N/5$; $y = 25.00$.

I.

Zero = 24.38 c.c.

<i>t.</i>	<i>a - x.</i>	<i>x.</i>	<i>k.</i>
120	21.30	3.08	0.001205
180	20.00	4.38	0.001217
255	18.67	5.71	0.001210
420	16.62	7.76	0.001112
480	15.92	8.46	0.001110
540	15.18	9.20	0.001135

$$k \text{ mean} = 0.001181$$

$$K = k \times 15/24.38 = 0.001211$$

II.

$$K \text{ mean} = 0.001200$$

Primary *isoalkyl* iodides are comparatively very inactive. *iso*Butyl iodide reacts slowly with practically all tried reagents, and, as in the present case, is less reactive than *iso*amyl iodide.

isoPropyl Iodide.

Each mixture contained 5 c.c. of *N*-isopropyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = $N/5$; $y = 25$.

I.

Zero = 22.85 c.c.

t .	$a-x$.	x .	k .
55	17.78	4.07	0.001962
165	16.56	5.29	0.001937
200	16.09	6.76	0.002108
225	15.40	7.45	0.002148
315	13.95	8.90	0.002024
400	12.40	10.45	0.002099

$$k \text{ mean} = 0.002046$$

$$K = k \times 25/22.85 = 0.002238$$

II.

$$K \text{ mean} = 0.002301$$

sec.-Butyl Iodide.

Each mixture contained 5 c.c. of *N-sec.*-butyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = $N/10$; $y=50$.

I.

Zero = 47.56 c.c.

t .	$a-x$.	x .	k .
100	38.69	8.87	0.002292
120	37.20	10.36	0.002319
200	32.75	14.81	0.002261
250	30.50	17.06	0.002250
310	28.10	19.46	0.002234
385	25.30	22.26	0.002285
400	24.95	22.61	0.002265

$$k \text{ mean} = 0.002272$$

$$K = k \times 50/47.56 = 0.002388$$

II.

$$K \text{ mean} = 0.002400$$

sec.-Amyl Iodide.

Each mixture contained 5 c.c. of *N-sec.*-amyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = $N/5$; $y=25$.

I.

Zero = 24.20 c.c.

<i>t.</i>	<i>a - x.</i>	<i>x.</i>	<i>k.</i>
100	19.93	4.27	0.002142
220	16.50	7.65	0.002114
300	14.88	9.32	0.002087
380	13.76	10.44	0.002001
450	12.67	11.53	0.002021
500	11.8	12.42	0.002101
625	10.45	13.75	0.002105

$$k \text{ mean} = 0.002081$$

$$K = k \times 25/24.2 = 0.002150$$

II.

$$K \text{ mean} = 0.002100$$

sec.-Hexyl Iodide.

Each mixture contained 5 c.c. of *N-sec.*-hexyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = $N/5$; $y = 25$.

I.

Zero = 23.00 c.c.

<i>t.</i>	<i>a - x.</i>	<i>x.</i>	<i>k.</i>
50	21.00	2.00	0.001904
100	19.36	3.64	0.001880
200	16.78	6.22	0.001853
290	15.04	7.96	0.001825
425	12.80	10.20	0.001875
500	11.90	11.10	0.001866

$$k \text{ mean} = 0.001867$$

$$K = k \times 25/23 = 0.002029$$

II.

$$K \text{ mean} = 0.002041$$

sec.-Heptyl Iodide.

Each mixture contained 5 c.c. of *N-sec.*-heptyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = $N/5$; $y = 25$.

I.

Zero = 23.80 c.c.

<i>t.</i>	<i>a - x.</i>	<i>x.</i>	<i>k.</i>
80	20.62	3.18	0.001926
100	20.00	3.80	0.001900
200	17.39	6.41	0.001843
280	15.70	8.10	0.001842
400	13.65	10.15	0.001860
600	11.35	12.45	0.001827

$$k \text{ mean} = 0.001866$$

$$K = k \times 25/23.8 = 0.001960$$

II.

$$K \text{ mean} = 0.002001$$

sec.-Octyl Iodide.

Each mixture contained 5 c.c. of *N-sec.-octyl iodide* and 5 c.c. of *N-sodium phenoxide*. Acid = $N/5$; $y=25$.

I.

Zero = 24.08 c.c.

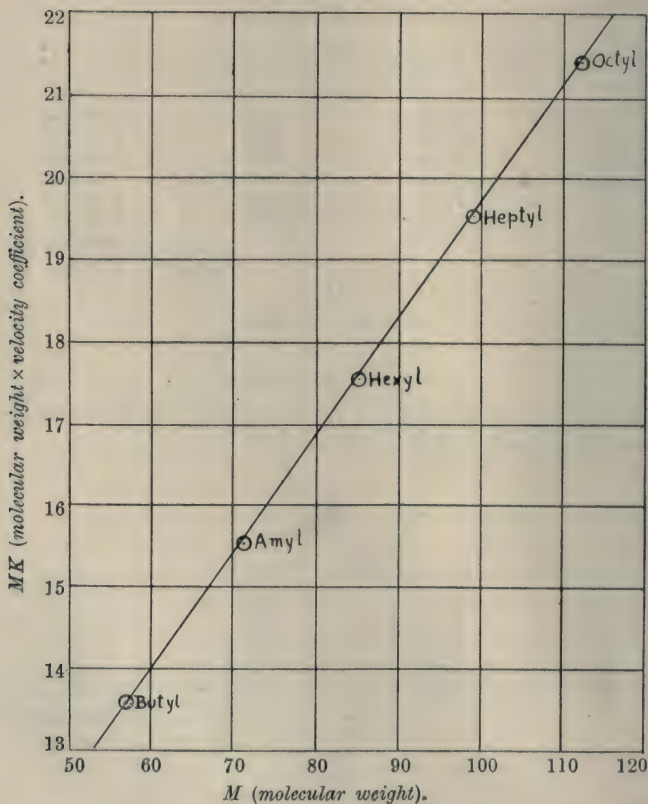
t .	$\alpha - x$.	x .	k .
120	19.70	4.38	0.001852
200	17.86	6.52	0.001824
240	16.64	7.44	0.001872
300	15.60	8.48	0.001816
380	14.00	10.08	0.001894
540	12.10	11.98	0.001834
600	11.53	12.85	0.001852

$$k \text{ mean} = 0.001849$$

$$K = k \times 25/24.08 \times 0.001919$$

II.

$$K \text{ mean} = 0.001908$$



The velocity-coefficients of the normal secondary alkyl iodides decrease regularly with increase in molecular mass. The graph (preceding page) obtained by plotting M (molecular weight of alkyl radicle) against MK (molecular weight of alkyl radicle \times velocity-coefficient) is practically a straight line, and the results are well represented by the equation $K = a + b/m$ (a and b are constants).

In this case $a = 0.001446$ and $b = 0.0521$.

*iso*Propyl iodide does not lie on the curve.

The following table shows the values of the velocity-constants found, compared with those calculated by means of the above equation:

	K_1 (calc.).	K (found).	$K - K_1$.
<i>iso</i> Propyl	0.002208	0.002657	+ 449
<i>sec.</i> -Butyl	0.002360	0.002388	+ 28
<i>sec.</i> -Amyl	0.002180	0.002150	- 30
<i>sec.</i> -Hexyl	0.002059	0.002029	+ 30
<i>sec.</i> -Heptyl.....	0.001972	0.001960	- 12
<i>sec.</i> -Octyl	0.001907	0.001919	+ 12

The comparative inactivity of *isopropyl* iodide is not surprising in view of the constants obtained for *iso*-compounds, although in *isopropyl* iodide the iodine is attached to the "secondary" carbon atom.

Both Wislicenus (*loc. cit.*) and Menshutkin (*loc. cit.*) find *isopropyl* iodide less reactive than *n*-propyl iodide. This result is confirmed by Wilderman (*loc. cit.*). On the other hand, Brusoff (*loc. cit.*) finds *isopropyl* iodide somewhat more reactive, and Burke and Donnan (*loc. cit.*) find *isopropyl* iodide enormously reactive as compared with *n*-propyl iodide. To see whether any olefine is formed in the case of secondary alkyl iodides experiments were made with the substances at the boiling point of alcohol, but as is the case with the primary *n*- and *iso*-alkyl iodides, no trace of olefine was obtained.

tert.-Butyl Iodide.

Each mixture contained 5 c.c. of *N*-*tert.*-butyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = $N/10$; $y = 50$.

I.

Zero = 32.00 c.c.

t .	$a - x$.	x .	k .
15	20.04	11.96	0.0398
20	18.48	13.52	0.0419
25	16.80	15.70	0.0436
30	14.00	17.90	0.0423
40	11.60	20.40	0.0439

k mean = 0.0423

$K = k \times 50/32 = 0.0661$

II.

K mean = 0.0612

tert.-Amyl Iodide.

Each mixture contained 5 c.c. of *N-tert.-amyl iodide* and 5 c.c. of *N-sodium phenoxide*. $\text{Acid} = N/10$; $y = 50$.

$$\text{Zero} = 30.16.$$

<i>t.</i>	$\alpha - x.$	$x.$	<i>k.</i>
5	27.00	3.16	0.03878
10	25.04	5.12	0.03405
15	23.80	6.36	0.02951
20	22.92	7.24	0.02652
30	21.90	8.26	0.02105

The olefine formed in the case of *tert.-amyl iodide*, that is, *isoamylene*, is a liquid, and evidently interferes with the course of the reaction, so that the "constant" diminishes as the reaction proceeds.

Tertiary alkyl iodides are very reactive towards sodium phenoxide, *tert.-butyl iodide* being twice as active as methyl iodide. The constants obtained are not very good owing to a disturbing side-reaction. Experiments showed that in the case of tertiary alkyl iodides heating with sodium phenoxide yielded olefines. In order to compare approximately the amounts of *isobutylene* obtained, *tert.-butyl iodide* in alcoholic solution was heated with alcoholic solutions of sodium ethoxide, sodium phenoxide, and sodium nitrophenoxide respectively, and the amounts of olefine obtained in each case are an interesting indication of the comparative effects of hydroxidion, ethoxidion, phenoxidion, and nitrophenoxidion on *tert.-butyl iodide*. The same apparatus was used for the purpose as that described by Brussoff (*loc. cit.*), and in each case equimolecular amounts of the reacting substances were taken, the maximum yield possible being, as in Brussoff's case, 300 c.c. The temperature was that of a surrounding jacket of boiling absolute alcohol, instead of boiling benzene as used by Brussoff.

The following table gives the results obtained:

Substance.	Yields of olefine, maximum 300 c.c. (0.760 mm.).
Potassium hydroxide (Brussoff)	245 c.c.
Sodium ethoxide	116 "
" phenoxide	94 "
" nitrophenoxide	76 "

The effect of the increasing electronegative character of the anion

is well shown. The present experiments do not support the deductions of Brussoff, for, if as he assumes, that in the constitution of secondary iodides the conditions are most favourable for elimination of hydrogen iodide and formation of olefine, or for what Nef describes as "alkylene" dissociation (*Annalen*, 1899, **309**, 126), then the secondary iodides should undergo this alkylene dissociation in the presence of alcoholic sodium phenoxide, since tertiary alkyl iodides certainly do so as shown above. This, however, is not the case; secondary alkyl iodides are shown to be even more stable than their primary isomerides.

Allyl Iodide.

Each mixture contained 10 c.c. of $N/10$ -allyl iodide and 10 c.c. of $N/10$ -sodium phenoxide. Acid = $N/20$; $y = 200$.

I.

Zero = 14.05 c.c.

t .	$a - x$.	x .	k .
10	11.82	2.23	0.01886
20	9.88	4.17	0.02110
25	9.16	4.89	0.02117
35	8.24	5.81	0.02014
40	7.92	6.13	0.01940
45	7.62	6.43	0.01913

$$k \text{ mean} = 0.01997$$

$$K = k \times 200/14.05 = 0.2843$$

II.

$$K \text{ mean} = 0.2881$$

On account of the very great reactivity of allyl iodide, it was only possible to work with $N/10$ -solutions at this temperature. The velocity-coefficient would undoubtedly have been larger if the measurements could have been made with N -solutions. Using the ratio obtained in a previous communication (*loc. cit.*) in the case of n -propyl iodide between K when N -solutions were employed and K when $N/10$ -solutions were measured, the velocity-coefficient for allyl iodide (assuming N -solutions) becomes approximately equal to 0.5240.

This, of course, entails the assumption that the ratio of $K(N/10):K(N)$ is the same in both cases.

General Conclusions.

(1) The relative reactivities of the alkyl iodides can be determined by measurements of their reaction-velocities with sodium phenoxide in alcoholic solution. Provided solutions of equal initial equivalent concentrations are used, a series of exact numbers is obtained which express among themselves the relative stabilities of the alkyl iodides.

Sodium phenoxide can therefore be regarded as a very suitable reagent with which to measure these relative reactivities.

(2) The *iso*-compounds are less reactive than the normal iodides.

(3) Secondary alkyl iodides are in all cases (except that of amyl iodide) somewhat less reactive than the corresponding normal primary isomeride. As in the case of the normal primary iodides, the velocity-coefficient of the normal secondary iodides decreases regularly with increase in molecular weight, and the relation between the velocity-coefficient and reciprocal of the molecular weight can be well expressed by a rectilinear equation.

(4) Tertiary alkyl iodides are the most reactive of the alkyl iodides, and with these a side-reaction takes place with elimination of hydrogen iodide and formation of olefine. The rate of reaction measured in this case is composite, and consists of (*a*) the rate of elimination of hydrogen iodide in presence of sodium phenoxide, and (*b*) the rate of formation of probably *p*-tert.-butylphenol (Lewis, T., 1903, **83**, 329). Both Wislicenus and Menschutkin were unable to determine any measurable reactivity for the tertiary iodides, and it would appear that, generally, if these compounds react at all they do so by the mechanism of "alkylene" dissociation.

(5) Allyl iodide is more reactive than any of the alkyl iodides. This substance has shown itself extremely active towards all reagents tried. It cannot be due altogether to the effect of unsaturation, since Wislicenus found vinyl iodide extremely slow.

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CLIV.—*The Change of Colour of Metallic Haloid Solutions.*

By CHARLES SCOTT GARRETT.

IT has long been known that the colour of the haloid salts of most coloured bases undergoes considerable changes, not only on concentration, but also on heating or on addition of foreign colourless haloids to their aqueous solutions, as well as on solution in non-aqueous solvents, such as alcohol. It has been pointed out by Müller (*Ann. Physik*, 1906, [iv], **21**, 515) that, although these four variants concentration, temperature, presence of colourless salts and change of solvent, produce similar changes of colour, yet the changes are not all exactly alike. It is evident, therefore, that more than one factor is at work in the production of these colour changes.

A considerable controversy has ranged around the question, and Donnan and Bassett in particular (T., 1902, **81**, 939), as the result of investigations on cobalt chloride solutions, have put forward the theory that the change of colour is due to formation of complex ions derived from salts of the type $R_2[CoCl_4]''$, and that the alteration in colour of copper and ferric haloid solutions is due to analogous changes.

On the other hand, several authorities take the view that the change is mainly one of dehydration, and amongst these the names of Russell (*Proc. Roy. Soc.*, 1881, A, **32**, 258), Hartley (*Sci. Trans. Roy. Dubl. Soc.*, 1900, **7**, 253), Engel (*Bull. Soc. chim.*, 1891, [iii], **6**, 239), Lewis (*Zeitsch. physikal. Chem.*, 1905, **52**, 224; 1906, **56**, 223), Jones (*Amer. Chem. J.*, 1911, **45**, 1, 113, and following numbers), and Houstoun (*Proc. Roy. Soc. Edin.*, 1911–13, **31**, 520; **32**, 41; **33**, 35, 137) must be mentioned.

In a later paper Donnan (*Zeitsch. physikal. Chem.*, 1905, **53**, 317) adopts an intermediate view, and suggests that the water molecules may be factors in the change, in that they may replace the halogen atoms, forming a series of compounds, including the non-ionised salt $(CuCl_2 \cdot 2H_2O)$, from which the following ions are derivable: $(Cu_4H_2O)^{++}$, $(CuCl_3H_2O)^+$, $(CuCl_3H_2O)^-$, $(CuCl_4)^{--}$. Later still, Denham (*Zeitsch. physikal. Chem.*, 1909, **65**, 641) has supported the theory of the complex salts by measurements of the transport numbers of the ions in the supposedly complex solutions. The transport values were found to become increasingly negative as the concentrations were increased, and Denham shows that this

can be explained if the salt undergoing electrolysis in the concentrated solution has a constitution of the type $\text{Cu}^{++}(\text{CuCl}_3)_2^-$.

The object of the present investigation was to approach the question from a somewhat different point of view. The change of colour must be viewed, not so much from the ionic point of view as from the point of view of a change in the constitution of the absorbing radicles, whether these are capable of ionisation or not. Experimental evidence supports the belief held also by several other investigators, amongst whom may be mentioned Houstoun (*Proc. Roy. Soc. Edin.*, 1913, **33**, 151) and Ball (*Proc. Roy. Soc.*, 1912, *A*, **87**, 138), that ionisation changes are not sufficient in themselves to explain many of the changes in colour and absorption which take place in solution on change of concentration.

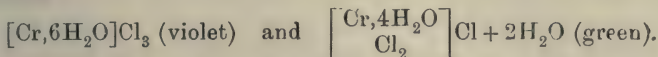
Donnan and Bassett first pointed out the relative nature of the changes in colour which take place on adding various colourless haloids, with a common ion, to the coloured haloid solution. The effect which they found has now been quantitatively examined, but instead of employing haloids which have an ion in common with the coloured haloid, ionic complications have been avoided as far as possible by the use of haloids giving rise to ions different from the halogen ion of the coloured solution. It will be seen from the following measurements of the molecular extinction of various copper bromide solutions that the change in absorption follows mainly the order of the electropositive character of the parent metal of the added haloid. The extinctions were measured for $\lambda = 652\mu\mu$ and at room temperature:

Solution.	Molecular extinction at $\lambda = 652\mu\mu$.
<i>N</i> -CuBr ₂ in <i>N</i> /4-HgCl ₂ solution	3.5258
<i>N</i> -CuBr ₂ in pure water	3.6114
<i>N</i> -CuBr ₂ in <i>N</i> -ZnCl ₂ solution	4.0710
<i>N</i> -CuBr ₂ in <i>N</i> -AlCl ₃ „	4.2628
<i>N</i> -CuBr ₂ in <i>N</i> -CaCl ₂ „	4.2724
<i>N</i> -CuBr ₂ in <i>N</i> -LiCl „	4.2788
<i>N</i> -CuBr ₂ in <i>N</i> -KCl „	4.2900
<i>N</i> -CuBr ₂ in <i>N</i> -HCl „	4.2933

In so far as the several hygroscopic chlorides of zinc, aluminium, lithium and hydrogen fall into their proper places in the order of their electropositive nature, no such special dehydrating or desolvating effect can here be ascribed to them as has been done by Jones and his co-workers (*Amer. Chem. J.*, 1908-12).

After the above result was obtained, the action of the same series of colourless chlorides on the change of colour of the chromium haloid was tried, because, in this instance, definite data as to the chemical changes which underlie the change of colour are at hand.

In this case the bluish-grey or violet colour of the dilute solutions which somewhat resemble neutral litmus changes to green in the case of the concentrated solutions, and it has been shown by Werner and Gubser (*Ber.*, 1901, **34**, 1379) and others that under ordinary conditions two configurations are stable enough to be obtained as solid hydrates from the solutions. These two crystalline forms, the one violet and the other green, are deemed to have constitutions which for the chloride can be represented as follows:



These constitutions have been arrived at by determinations of the amount of chlorine that can be precipitated as silver chloride, as well as from the behaviour of the various water molecules to dehydrating agents, and they are now generally accepted as correct. Thus, in the case of the chromium haloids, a change of colour takes place, and it is known that a complex metallic radicle is produced on concentration or on heating, and although the interchange from one form to the other is slow, a matter of weeks at the ordinary temperature according to Roozeboom and Olie (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 66), it is possible, by allowing sufficient time, to estimate the ultimate relative effects of colourless haloids on this reaction.

The results that were obtained with chromium bromide are not quite so consistent as in the case of copper bromide, but in general they seem to indicate the reverse order of effect to that which obtains in copper bromide solution. The molecular extinctions were measured in solutions 0.842*N* with respect to Cr, for $\lambda = 630\mu$ at room temperature, approximately three days and two and a-half months after making up the solutions:

Solution.	Molecular extinction after 3 days.	Molecular extinction after 2½ months.
CrBr ₃ in <i>N</i> /4-HgCl ₂	2.064	2.166 (2.472) *
CrBr ₃ in <i>N</i> -AlCl ₃	2.506	2.258
{ CrBr ₃ in <i>N</i> -LiCl	2.236	2.219
{ CrBr ₃ in <i>N</i> -CaCl ₂	2.230	2.212
CrBr ₃ in <i>N</i> -KCl	2.112	2.180
CrBr ₃ in <i>N</i> -ZnCl ₂ ..	2.488	2.177 (?)
CrBr ₃ in <i>N</i> -KBr	2.191	2.123
CrBr ₃ in water	2.064	2.064

* Estimated for *N*-mercuric chloride solution which cannot be obtained owing to insolubility of the salt.

It will be seen from the above table that although at first no apparent regularity is obtained, yet after the equilibrium has been established (at the end of two and a-half months) the more electropositive chlorides have in general the least effect, that is to

say, the action in this case is just the reverse of that found with copper bromide solution. Zinc chloride has an exceptionally low end value, although at first a high value of extinction was obtained. What the cause of this exceptional behaviour may be it is difficult to say, but it is very possible that excessive hydrolysis and production of free acid has taken place, and that the low value is due to this cause. The calcium chloride and lithium chloride solutions appear to have practically identical effects both here and in the case of the copper bromide solution.

If now the time change be examined somewhat more closely, it will be seen that the molecular extinctions in the presence of each of the hygroscopic chlorides start with a high value, and then decrease, whilst in the case of the non-hygroscopic chlorides the extinctions start at a low value and then increase.

Now, all the solutions were made up from the same concentrated parent solution by adding solutions of the colourless chlorides and diluting the mixtures to the required volumes. Hence it would appear as if the water molecules play an initial part in changing the complex to the simple configuration, and that following this a second reaction sets in tending again to the formation of complexes owing to the presence of the colourless haloids in the solutions. When, however, the colourless haloids have decidedly dehydrating properties, the hydration on dilution is initially inhibited, although the final point reached, there being excess of water molecules present, is independent of the hygroscopic properties of the colourless haloid.

The solutions were preserved for the final readings in stoppered bottles to avoid the possibility of concentration. The constancy of the pure aqueous solution after three days indicates a quicker attainment of the equilibrium than Roozeboom and Olie observed. These authors, and recently Byk and Jaffe (*Zeitsch. physikal. Chem.*, 1910, **68**, 328) also, noticed an inhibiting action in the case of the chloride solution when hydrogen chloride was present. Although this inhibition and displacement of the equilibrium by hydrogen chloride has been confirmed, yet it appears probable from the following values that this displacement decreases to a final value which is less than that produced by other chlorides.

Solution.	Molecular extinction, λ 630 $\mu\mu$.		
	After 3 days.	After 10 days.	After 2½ months.
CrBr ₃ in <i>N</i> -HCl	3.066	2.884	2.251
CrBr ₃ in <i>N</i> -HNO ₃	2.840	2.088	1.984

In the case of the nitric acid solution the colour produced was a reddish-brown, and very different from that of the other chromium

solutions, and it is therefore obvious that some special chemical transformation has taken place in the solution, doubtless the production of free bromine from the decomposition of the hydrogen bromide liberated.

It was thought that possibly the change of colour of the copper haloid on dilution might partake of the nature of a time reaction in some slight degree. The measurements of the molecular extinction, however, of an aqueous solution of pure cupric bromide immediately after making up and two and a-half months later gave the respective values 3.5904 and 3.5916 for $\lambda = 652\mu\mu$, hence it must be concluded that the equilibrium of the copper solutions is reached instantaneously.

Again, the change of colour appears to be proportional to the amount of foreign salt present in the solution, whether this is capable of producing chemical action or not, as the following figures show:

<i>N</i> -CuBr ₂ in H ₂ O	3.6114	>0.6674		<i>N</i> -CuBr ₂ in H ₂ O	3.6114	>0.6626
<i>N</i> -CuBr ₂ in <i>N</i> -LiCl ...	4.2788			<i>N</i> -CuBr ₂ in <i>N</i> /4-H ₂ SO ₄	3.5488	
<i>N</i> -CuBr ₂ in 2 <i>N</i> -LiCl..	4.9462			<i>N</i> -CuBr ₂ in <i>N</i> /2-H ₂ SO ₄	3.4888	

This fact is only another indication that changes of colour are not directly dependent on ionisation changes, for, in general, the addition of a second amount of a foreign substance does not produce a change in ionisation equal to that consequent on the first addition of the same amount.

The changes produced by various other salts in the case of copper bromide have been measured, and the results are included in the following table:

Solution.	Molecular extinctions ($\lambda = 652\mu\mu$).	Solution.	Molecular extinctions ($\lambda = 652\mu\mu$).
<i>N</i> -CuBr ₂ in H ₂ O	3.6114	<i>N</i> -CuBr ₂ in <i>N</i> -HNO ₃	4.0328
<i>N</i> -CuBr ₂ in saturated (<i><N</i>)-Na ₂ SO ₄	3.4336	<i>N</i> -CuBr ₂ in <i>N</i> -KBr	4.1700
<i>N</i> -CuBr ₂ in <i>N</i> /4-K ₂ SO ₄ ...	3.5182	<i>N</i> -CuBr ₂ in <i>N</i> -KCl	4.2900
<i>N</i> -CuBr ₂ in (<i><N</i> /4)-KClO ₄	3.6268	<i>N</i> -CuBr ₂ in <i>N</i> -HCl	4.2933
<i>N</i> -CuBr ₂ in <i>N</i> -KNO ₃	3.8796	1.194 <i>N</i> -CuBr ₂ in H ₂ O	4.3096

The change of absorption occasioned by the presence of various acidic radicles in the bromide solution follows an order of decreasing intensity corresponding with [Cl], [Br], [NO₃], [ClO₄], [SO₄], which agrees very well with the order found on a previous occasion (*Zeitsch. Elektrochem.*, 1913, **19**, 1) for the influence of the acidic radicles on the absorption of the [Cu] radicle. Nitric acid, like hydrochloric acid, has a greater effect than its potassium salt, but here again the colour of the solution appeared to be abnormal, as in the parallel case of chromic bromide solution, and a similar explanation doubtless applies. Solution in *N*-hydrochloric acid

increases the extinction to a value practically equivalent to that obtained on raising the normality of the copper bromide solution from 1 to 1.194*N*.

An indication of the nature of the changes which other haloid solutions such as those of cobalt, nickel, iron, and manganese undergo can be gained by a consideration of the colour sequences which are followed on the dehydration of their hydrated salts, and for brevity these may be tabulated as follows:

Chlorides.

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, green \rightarrow CuCl_2 , black
 \rightarrow dilute aqueous solution, light blue.

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, dark red \rightarrow $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$,
 dark blue \rightarrow CoCl_2 , violet-blue \rightarrow
 dilute aqueous solution, pink.

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, green \rightarrow \rightarrow
 NiCl_2 , yellow \rightarrow dilute aqueous
 solution, greenish-yellow.

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, yellow \rightarrow $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$,
 brown \rightarrow FeCl_3 , black \rightarrow dilute
 aqueous solution, light yellow.

$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, light pink \rightarrow $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$,
 darker pink \rightarrow MnCl_2 , reddish-pink
 \rightarrow dilute aqueous solution, very light
 pink.

$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, green or greyish-blue \rightarrow
 $\text{CrCl}_3 \cdot 4\text{H}_2\text{O}$, green \rightarrow CrCl_3 , peach
 or blood-red \rightarrow dilute aqueous solu-
 tion, bluish-violet.

Sulphates.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, blue \rightarrow CuSO_4 , white \rightarrow
 dilute aqueous solution, light blue.

$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, dark red \rightarrow CoSO_4 , rose-
 red \rightarrow dilute aqueous solution,
 pink.

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, green \rightarrow NiSO_4 , faint
 and yellowish \rightarrow dilute aqueous
 solution, greenish-yellow.

Basic iron sulphates, yellow \rightarrow $\text{Fe}_2(\text{SO}_4)_3$,
 white \rightarrow dilute aqueous solution,
 light yellow.

$\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$, light pink \rightarrow MnSO_4 ,
 $4\text{H}_2\text{O}$, lighter pink \rightarrow MnSO_4 , white
 \rightarrow dilute aqueous solution, very
 light pink.

$\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, violet \rightarrow $\text{Cr}_2(\text{SO}_4)_3$,
 $6\text{H}_2\text{O}$, green \rightarrow $\text{Cr}_2(\text{SO}_4)_3$, peach or
 blood-red \rightarrow dilute aqueous solution,
 bluish-violet.

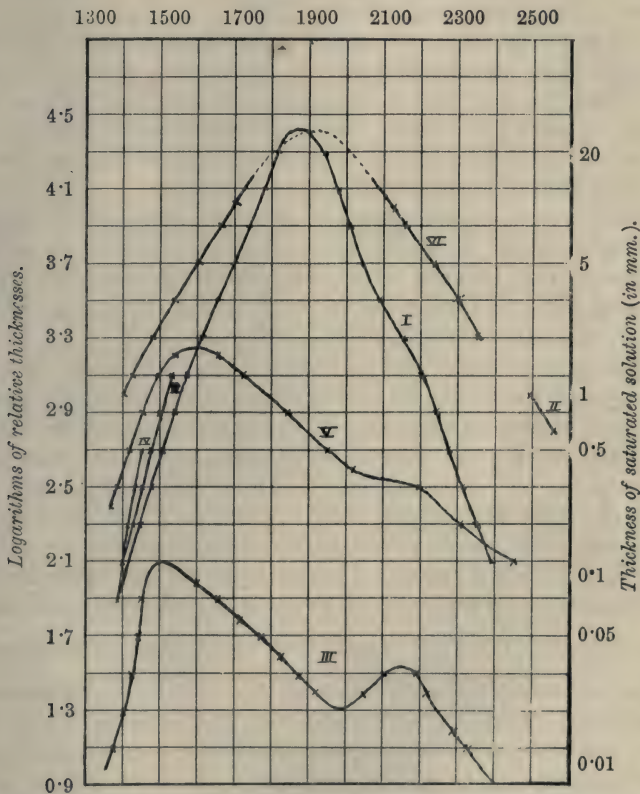
Now in all the above cases of the chlorides the dehydration of the solid hydrates produces changes in colour which indicate that the absorption boundaries move in the opposite direction to that in which they would move if the colour approached the colour of the dilute aqueous solution. As the dilute aqueous solutions do not contain the complex form of the salts, it may be assumed that in passing from the hydrated to the anhydrous solid chloride formation of complexes takes place. On the other hand, the sulphate dehydration sequence shows a movement of the absorption limits towards, and sometimes, as in the case of cupric, ferric and manganese sulphates, past the limit for the dilute solutions, so that here formation of complexes is probably absent. Chromium sulphate alone is an exception, and, judging from its dehydration colour sequence, there would appear to be formation of complexes. This fact would permit a distinction to be made between the various colour changes, and ally those of cobalt, nickel, iron, and manganese salts with those of the copper salts. In all these derivatives the colour change is therefore due to the formation of complex acidic radicles.

It is a noteworthy fact that all the metallic radicles in the haloid

solutions of which formation of complexes appears to take place exhibit a tendency to variable valency. On the contrary, neodymium and praseodymium, the haloid solutions of which do not undergo much change of colour on alteration of the several variants (Stahl, *Le Radium*, 1909, **6**, 216; Ball, *ibid.*; Schaefer, *Physikal.*

FIG. 1.

Oscillation frequencies.



{	I.	Saturated CuCl_2 solution in water.	{	III.	Saturated CuBr_2 solution in water.
	II.	100 CuCl_2 „ „		IV.	100 CuBr_2 „ „
		{	V.	Saturated NiBr_2 solution in water.	
		{	VI.	10 NiBr_2 „ „	

Zeitsch., 1906, **7**, 822, etc.), do not show any tendency to function in varying valencies.

An attempt has been made to discover bands due to the complex radicles by photographing saturated solutions of various haloids. As such saturated solutions are very opaque, especially bromide

solutions, it was necessary to photograph them in very thin layers, and for this purpose advantage was taken of a quartz absorption cell recently constructed for this laboratory with which layers down to 1/1000 mm. thickness can be obtained. The results are shown on the curves in Figs. 1 and 2, together with the absorption spectra of the same solutions after dilution to 10 or 100 times their volume for purposes of comparison. These saturated solutions all possess a very high normality; thus, for instance, the aqueous ferric chloride solution was approximately 13*N*.

The change from the saturated to the dilute solution is throughout exceedingly noticeable, but only in the case of cupric bromide, cupric chloride, and nickel bromide solutions have indications of selective absorption bands due to the complex radicles been obtained, and the maxima of these bands are situated at $\lambda = 1975$, 2100, and 2100 $1/\text{\AA}$ respectively.

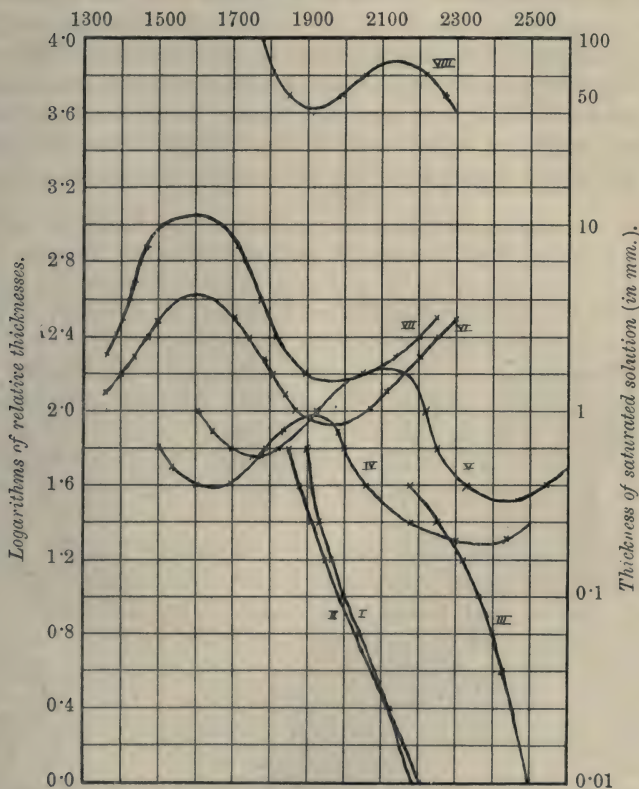
The saturated cupric bromide solution very much resembled liquid bromine or a concentrated alcoholic solution of iodine in appearance, and, like the latter, was practically opaque to light in these regions. As seen from curve III, Fig. 1, a layer of about 0.1 mm. thickness absorbs all the light rays.

The absorption band on the redward side culminates in a maximum beyond the limits of the visible and situated approximately at 800 $\mu\mu$. Hydrated solid cupric salts and their solutions owe their blue colour mainly to this absorption band, and as has been pointed out, notably by Hantzsch (*Ber.*, 1908, **41**, 4328) and Poma (*Gazzetta*, 1910, **40**, i, 176), this blue colour is very probably connected with the complex radicle $[\text{Cu}, 4\text{H}_2\text{O}]$ present in all these states of the cupric salts. If now three of the water molecules of this radicle are replaced by bromine (or chlorine) the negative complex radicle $[\text{Cu}^{\text{Br}_3}_{\text{H}_2\text{O}}]$ postulated by Denham is obtained, and it is not improbable that the new band at 1950 $1/\text{\AA}$ represents this replacement. Further, the situation of this band at a point much nearer the violet than the original $[\text{Cu}, 4\text{H}_2\text{O}]$ complex band can be regarded as due to the greater strength of the valency fields between bromine and copper than those between water and copper. This view would also explain why the indication of a band for the $[\text{Cu}^{\text{Cl}_3}_{\text{H}_2\text{O}}]$ complex is situated a little nearer still to the violet at 2100 $1/\text{\AA}$, for the valency field between copper and chlorine will be stronger than that between copper and bromine. The great increase of absorption in the red regions of the copper bromide solution on concentration can thus be explained as due to the replacement of three molecules of $[\text{Cu}, 4\text{H}_2\text{O}] = \text{Cl}_2$ by the molecule

$[\text{Cu}, 4\text{H}_2\text{O}] = [\text{Cu} \begin{smallmatrix} \text{Cl}_3 \\ \text{H}_2\text{O} \end{smallmatrix}]$. The ordinary $[\text{Cu}, 4\text{H}_2\text{O}]$ band at $800 \mu\mu$ should remain intact, but probably be decreased in intensity, whereas the new complex acid radicle now superimposes a great increase of absorption higher up in the visible red regions. It is quite possible also that the complex acid radicle may help to main-

FIG. 2.

Oscillation frequencies.



- { I. Saturated FeCl_3 solution in water.
 { II. FeCl_3 (anhyd.) in EtOH .
 { III. 100 FeCl_3 solution in water.
 VIII. MnCl_2 " "

- { IV. Saturated CrBr_3 solution in water.
 { V. 100 CrBr_3 " "
 { VI. CoCl_2 solution in water.
 { VII. 10 CoCl_2 " "

tain the intensity of absorption in the original $800 \mu\mu$ band, but there was no opportunity of testing this.

The change of absorption in the concentrated chromic bromide solution is of a rather different character from that which occurs in the copper solutions. The total absorption is not nearly so much

increased, but the two bands (Fig. 2, curve IV) experience a very evident shift to the redward side. No indication was obtained of the third band lower down in the red which has been noted by some observers,* but it was found instead that no effect could be produced on the photographic plate by passing light through 1 mm. of the liquid for seventy-five minutes.

In the concentrated solution the absorption minimum seems to have been flattened to some extent, and this would lead to the conclusion that the band in the region $2400\ 1/\text{\AA}$ had been moved relatively nearer the lower band, or possibly that fresh but not very intense absorption was superimposed at the minimum point. The latter occurrence would explain an apparent redward displacement of the band at $1650\ 1/\text{\AA}$, so that the change in the band and in the minimum could be attributed to the change from the radicle $[\text{Cr}, 6\text{H}_2\text{O}]$ to the radicle $[\text{Cr}^{\text{Br}_2}_{4\text{H}_2\text{O}}]$. Further, as the latter radicle would be less electropositive than the former, it could be assumed that the valency field between it and the ionisable bromine atom would not be so strong as it was originally. Consequently, if the band at $2400\ 1/\text{\AA}$ corresponded with this field, it would undergo a redward displacement on complex formation.

It is interesting to note in this connexion that Luther and Nikolopulos (*Zeitsch. physikal. Chem.*, 1913, **82**, 362) have obtained a displacement towards the red of the green band of cobalt solutions containing the complex $[\text{Co}(\text{NH}_3)_6]$ radicle when the ammonia molecules are replaced by acid groups such as (NO_3) , (Cl) , and (Br) .

The ultra-violet end-absorption of a saturated solution diluted 100 times of the violet chromium bromide was examined in the ordinary manner, and found to be considerably less than that of the green solution of the same concentration, and from which it was derived. A green solution in hydrochloric acid of the same concentration had a still greater end-absorption. These ultra-violet absorption changes can be understood if absorption in this region is attributed to the actual chromium atom, which, as complex formation sets in, becomes more opened up and thereupon produces greater absorption. The ultra-violet end-absorption of copper salts behaves in a corresponding manner, and therefore can be attributed analogously to the state of the copper atom in the molecule.

None of the bands mentioned by Hiebendaal (*Proefschrift, Amsterdam*, 1873) or by Russell and Orsman (*Chem. News*, 1889, **59**, 93) was obtained in a saturated ethyl alcohol solution of anhydrous ferric chloride, nor do any bands appear to be present

* Kayser's "Handbuch," 1905, III, 402.

in a saturated aqueous solution as far as investigated. The dilute solution of manganese bromide possessed too little absorption to be shown on the same scale as the saturated deep pink solution. This solution also, on keeping, gradually changes to a brown colour. Hartley (T., 1912, **101**, 826) has observed a change of colour of the sulphate solution to a yellow shade on keeping, and has attributed it to the formation of colloidal manganic hydroxide, $\text{MnO}(\text{OH})_2$. It is probable that here the same reaction is taking place, complicated by the simultaneous production of hydrogen bromide or bromine.

The saturated solution of chromic chloride had a very dark green colour, whilst the saturated solution of nickel bromide was dark brown, very opaque, and of a syrupy consistency. The concentrated solution of cupric chloride was still green and transparent, and the saturated solution of cobalt chloride possessed a deep, plum-red colour.

EXPERIMENTAL.

All the materials used were the purest obtainable. Concentrated solutions of both copper and chromium bromide were made up, and equal amounts of these were measured with the same pipette and diluted to the requisite volumes. The various colourless haloids were dissolved to known concentrations, and where the salts were too deliquescent to permit of accurate weighing out, the solutions were estimated. Before use the aluminium chloride was distilled until a colourless sample was obtained. The copper solution was estimated volumetrically by the potassium iodide and sodium thiosulphate method, and the similar chromium solution by precipitation of the hydroxide.

Extinctions were measured by Hilger's improved modification of the Hüfner spectrophotometer in a manner already described (*Zeitsch. Elektrochem.*, 1913, **19**, 1), and the concentrations of the solutions were so arranged that values of α in the neighbourhood of 80° were obtained, since experience showed that the sensitivity of the instrument was much greater at high extinctions.

The saturated solutions were prepared by repeated shaking at the room temperature until no more solid dissolved, and after filtration, a very slow process with these viscous solutions, they were photographed in the micro-cell, using a Nernst lamp as the source of light. In order to allow measurements of the absorption limits to be made in the continuous spectrum of the Nernst lamp, a glass quarter wave-plate was inserted between the cell and the slit, and the interference fringes appearing on the plate were calibrated by photographing alongside at the beginning and end of each plate the

spectrum of a hydrogen-neon tube, and the prominent lines at 6562, 5853, and 4861 Å were used as graduation lines. The Nernst source permitted the total red sensitivity of the Wratten and Wainwright panchromatic plates to be utilised, but the glass quarter wave-plate greatly reduced the light intensity besides cutting off the ultraviolet rays, making it necessary to give exposures of at least ten minutes.

Conclusions and Results.

(1) The colour changes of the solutions of the haloid salts of copper and chromium on concentration, etc., whilst of much the same nature optically, are due to the increasing formation of complex radicles of opposite kinds, acidic and metallic respectively, but in both changes the solvent must be regarded as taking some part.

(2) The analogous changes in cobalt, nickel, ferric and manganous haloid solutions are probably of the same type as that of the copper solutions.

(3) The determining cause of the changes lies chiefly in the tendencies of these metallic radicles to exhibit variations in the type of their valencies in contra-distinction to the neodymium and praseodymium radicles where no such tendency appears to be present.

(4) In the case of the complex chromium haloids some configurations have a stability sufficiently great to allow the actual complex salts to be obtained from the complex solutions. Moreover, the change from simple to complex is here so slow as to be a time reaction in which water plays the initial part.

(5) On the contrary, the colour changes of copper solutions are not time reactions, and the solvent probably plays a secondary part.

(6) For copper bromide solutions in which acids or foreign salts are present the change of colour is, within limits, proportional to the content of acid or colourless salt.

(7) Indications of selective absorption bands due to complex radicles have been obtained in the saturated solutions of cupric chloride, cupric bromide, and nickel bromide.

In conclusion, I wish to express my indebtedness to Professor Baly for the many facilities that he has afforded me for the carrying out of this research, as well as for the kindly interest which he has shown throughout the course of the work.

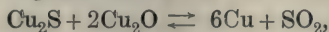
CLV.—*The Action of Sulphur Dioxide on Copper at High Temperatures.*

By CLIFFORD MORGAN STUBBS.

WHILST engaged recently on a spectro-photometric measurement of the emissivity of solid and liquid copper, the author's attention was drawn to a remarkable result communicated by Sieverts and Krumbhaar (*Zeitsch. physikal. Chem.*, 1910, **74**, 277) in a paper on the behaviour of that metal towards gases. They found that the solubility of sulphur dioxide in molten copper was proportional to the square root of the pressure of the gas, a law which also holds for the solution of diatomic elementary gases such as hydrogen or oxygen in copper and other metals. Whilst for such gases, however, the behaviour may, by the well-known theory of van't Hoff, be explained by their dissolving monatomically, this explanation is impossible for sulphur dioxide in copper. Sieverts and Krumbhaar remarked on this, and even raised the question whether the square root law is not characteristic of all metallic solutions of gases, and whether the usual explanation (as above) may not be wrong. They proposed to investigate further the solubility of other non-elementary and of monatomic elementary gases; and they suggested that measurement of the depression of the freezing point of copper by dissolved sulphur dioxide might illuminate the question. Such a measurement has not been made since their paper appeared; and as the author happened to be using in his research an apparatus in which hydrogen was being bubbled through molten copper, closed from the atmosphere, and in which the temperature of the metal was very accurately read by means of a thermo-couple, it seemed worth replacing the hydrogen by sulphur dioxide and determining the depression of freezing point caused thereby. From this beginning, and on account of the nature of the results obtained, the research has considerably extended, and includes an investigation of the equilibrium between sulphur dioxide and solid copper, solid cuprous sulphide, and solid cuprous oxide.

The previous data may be briefly summarised as follows: Sieverts and Krumbhaar (*loc. cit.*) have shown that molten copper dissolves sulphur dioxide in relatively large quantities—about twelve volumes at the melting point and under atmospheric pressure. They measured the solubility at five temperatures, from 1123° to 1327°, and found that it increased considerably with rise of temperature. By extrapolation, the solubility under

atmospheric pressure at the melting point would be about 0.422 gram per 100 grams of copper, decreasing with fall of temperature at the rate of about three-quarters of a milligram per degree. At constant temperature and varying pressures (up to 1000 mm.) the quantity \sqrt{p}/m , where p denotes pressure and m the amount of sulphur dioxide dissolved per unit mass of copper, was approximately constant, a general tendency for the values to fall off at the lower pressures being attributed to experimental errors. The gas could be pumped off under diminished pressure, the last residue being removed only by prolonged exhaustion, but evolved immediately on the copper solidifying, the gas being insoluble in the solid metal. Heyn and Bauer (*Metallurgie*, 1906, **3**, 82) had previously shown that sulphur dioxide was without action on solid copper between 900° and 1100°, and that copper freezing from a solution of the gas in the molten metal contains occluded sulphur dioxide, but practically no sulphide. In a paper which appeared during the course of the present research, Schenck and Hempelmann (*Metall. u. Erz.*, 1913, **1**, 283) show that the reaction between sulphur dioxide and solid copper, solid cuprous sulphide, and solid cuprous oxide,



is an interesting case of equilibrium in a univariant system, a definite pressure of sulphur dioxide corresponding with each temperature. This pressure was found to be one atmosphere at 730°, and increased rapidly with temperature. Hence they explain the lack of action of sulphur dioxide on solid copper at high temperatures, shown by Sieverts and Krumbhaar, and by Heyn and Bauer, as due to the pressure of gas being too low. In an extensive theoretical discussion of the nature of the reactions which play a part in the smelting of copper sulphide ore, they show that the above equilibrium equation (the solid phases being now replaced by a liquid one, and the system in general trivariant) affords a satisfactory explanation of observed phenomena; and they assume that the solution of sulphur dioxide in copper is wholly due to the formation of cuprous oxide and cuprous sulphide.

In another recent paper, which came to the author's notice only shortly before the conclusion of his work, Sieverts and Bergner (*Zeitsch. physikal. Chem.*, 1913, **82**, 257) describe further experiments on the solution of sulphur dioxide in molten copper. They find that whilst the addition of a noble metal decreases the solubility of sulphur dioxide, this occurs much more when cuprous oxide or cuprous sulphide is added; and that with increasing concentration of either of these substances the expression \sqrt{p}/m is no longer constant, but the relation approximates more to

Henry's law. They conclude that the results point to at least a partial formation of cuprous sulphide and cuprous oxide from the dissolved sulphur dioxide, but leave the matter still in some doubt, the greatest difficulty being the existence of the proportionality of \sqrt{p} and m discovered in the former research.

PART I.—Nature of the Solution of Sulphur Dioxide in Copper.

When the present research was commenced the latter two papers had not appeared, and the author's object in measuring the depression of the freezing point of copper by sulphur dioxide was to test whether twice the normal depression would be given, in correspondence with van't Hoff's theory and Sieverts and Krumbhaar's determined constancy of \sqrt{p}/m , and possibly indicating an ionisation of sulphur dioxide into two ions in the metallic solvent. The original apparatus consisted of a closed vertical iron tube 5 cm. in internal diameter, which surrounded the copper contained in a tall, unglazed porcelain pot, through the top of which passed a thermo-couple tube and silica tubes for inlet and outlet of gas. The iron tube was itself wound with resistance wire for heating purposes, and placed inside a large platinum-wound electric furnace. In the first experiment it was found that the sulphur dioxide rapidly attacked the heated parts of the iron tube; and owing to fear of disturbing influences from this source, and also to the fact that the "nichrome" winding on the iron tube was liable to frequent breakdown at the temperatures employed, the copper in all subsequent experiments was contained in a thick-walled porcelain pot, which was closed with a cemented-on lid pierced to admit closely-fitting thermo-couple and gas tubes, placed in a small platinum-wound resistance furnace and packed tightly round with kieselguhr. When no current of gas was passing, the metal in the pot was slowly oxidised through the gradual diffusing in of air, but when (as usual) a brisk current was passing such oxidation was very slow, if it occurred at all. The gas-inlet tube extended nearly to the bottom of the metal, which was about 5 cm. in depth. The gases used (namely, hydrogen, nitrogen, carbon dioxide, sulphur dioxide, and air) were thoroughly dried, and were free from harmful impurities such as hydrogen sulphide. The gas reservoirs and connexions were so arranged that one gas could be passed after another without a break, and that two gases could be simultaneously passed. A stream of bubbles, at the rate of about six a second, was kept passing through the metal, thus securing both rapid equilibrium and (by their stirring action) the best conditions for the taking of cooling curves. A fresh amount of pure electrolytic copper, from 300 to 400 grams, was used in

each experiment. The thermo-couple was inserted 3 or 4 cm. below the surface of the metal. It was composed of platinum and platinum-rhodium, and was standardised against the known melting points of antimony, silver, and copper. Its indications were read by means of an accurately calibrated potentiometer reading directly to 1 microvolt, that is, about 0.077° . A means of continually compensating for the small fluctuating thermal *E.M.F.* originating in the instrument allowed great accuracy in measuring the *E.M.F.* of the thermo-couple, the error of a reading being not more than a microvolt. This compensation-apparatus, as well as the iron tube, potentiometer, etc., are fully described in the author's paper on the emissivity of copper (*Proc. Roy. Soc.*, 1913, *A*, **88**, 195).

The following is a summary of the four trustworthy experiments from which the results to be discussed are deduced:

1. (a) A mixture of hydrogen and carbon dioxide was passed until the copper melted; then carbon dioxide was passed alone. Successive potentiometer readings for the melting point were 11.121 and 11.120 millivolts. (b) Sulphur dioxide was passed for 35 minutes; the reading for the melting point was 10.9525; after passing further 75 minutes the reading was 10.9505.

2. (a) Carbon dioxide and hydrogen were passed until the copper melted, then hydrogen alone for 17 minutes; the reading was 11.112. Hydrogen was then passed for 27 minutes, when the reading was 11.114. (b) Carbon dioxide was passed for 20 minutes, when the reading was 11.110; after a further 40 minutes the reading was 11.106. (c) Sulphur dioxide was passed for 34 minutes, when the reading was 10.9425; second and third readings gave 10.9445. (d) Carbon dioxide was passed for 100 minutes, when the reading was 11.031. (e) Hydrogen, after being passed for some time, gave the reading 11.086.

3. (a) Carbon dioxide, after being passed, gave the reading 11.0675; probably some oxide was present. (b) Hydrogen, after passing for 17 minutes, gave the reading 11.101; after a further 23 minutes, 11.127; after a further 27 minutes, 11.126. (c) Carbon dioxide, after passing for 18 minutes, gave the reading 11.125; after a further 22 minutes, 11.124; after a further 20 minutes, 11.121; and after a further 21 minutes, 11.119. (d) Sulphur dioxide, after passing for 32 minutes, gave the reading 10.9455; after a further 51 minutes, 10.9435. (e) Hydrogen and a little sulphur dioxide were passed until the reading, which on the first passing of hydrogen rose to 11.051, fell to 10.9875. (f) Carbon dioxide was passed for 1 hour to expel hydrogen; sulphur dioxide was then passed, when, after 48 minutes, the reading was 10.915.

4. (a) Hydrogen was passed for a considerable time, when read-

ings of 11.100, 10.099, and 11.100 were obtained. (b) Nitrogen, after being passed for 26 minutes, gave the reading 11.0965; after a further 24 minutes about the same reading was obtained; after a further 23 minutes the reading was 3 or 4 microvolts lower (the cooling curve was not a very good one). (c) Air was passed for 12 minutes, when the reading was 10.94; air was further passed for 3 minutes, then carbon dioxide. (d) Carbon dioxide, after being passed, gave the first halt at 10.9045; the readings gradually fell to 10.8405, when they became constant. Further passing of carbon dioxide gave the first halt at 10.9055; the readings fell, and became constant at 10.8375. (e) Sulphur dioxide was passed for 28 minutes; the first halt was given at 10.857; the second constant halt was not determined. After a further 36 minutes the first halt was recorded at 10.8435 (rather doubtful); and the second constant point at 10.8105.

In order to draw definite conclusions from the above results it must first be decided what reading is to be taken as corresponding with the true freezing point of copper. In the first three experiments, after reducing any oxide with hydrogen, carbon dioxide, described by Sieverts and Krumbhaar as insoluble in copper, was passed to sweep out the former gas prior to passing in sulphur dioxide, a portion of which would otherwise have been reduced, with the formation of cuprous sulphide. Experiments 1(a), 2(b), and 3(c) show that the freezing point became very slowly but steadily lower with increasing time of passing carbon dioxide. This is attributable either to a small diffusion of oxygen into the copper, or more probably to a slow oxidising action of the carbon dioxide, the oxygen dissociation pressure of which at 1083° is, although small, greater than that of a dilute solution of cuprous oxide in copper. In experiment 4(b) nitrogen was passed after the hydrogen, but even this gave a small depression compared with the reading for hydrogen. The solubility of hydrogen in copper should, if the metal separated in the pure state, give a calculated depression of 0.45°; but as a solid solution containing three-fourths of the hydrogen separates (Sieverts and Krumbhaar, *loc. cit.*) the depression would be less, and might even become an elevation. The value of the freezing point of copper in hydrogen is probably to within one- or two-tenths of a degree that for the pure metal, the above experiments showing that no higher value could ever be obtained by sweeping out the hydrogen, whilst there is no evidence of the value being to any extent lower. The actual value obtained differs slightly in the several experiments, due to varying positions of the thermo-couple.

The thermo-couple calibration showed that each microvolt depres-

sion on the potentiometer corresponded with 0.077° . It remains, however, to determine the constant E to be used in the formula

$$t = Em,$$

where t denotes depression in degrees, and m the concentration of the solution, measured in gram-molecules per 100 grams of copper. (This way of expressing concentration is used throughout.) From the heat of fusion of copper, 43.3 calories according to Richards and Frazier (*Stahl. u. Eisen*, 1894: quoted by Heyn, *Zeitsch. anorg. Chem.*, 1904, **39**, 1), E for dilute solutions is given by van't Hoff's well-known formula:

$$E = \frac{1.985 T^2}{100w},$$

where w = latent heat of fusion, and T = the absolute temperature of the melting point. According to this, $E = \frac{1.985 \times 1356^2}{100 \times 43.3} = 843$.

This value is, however, dependent on the somewhat uncertain value of w . E can also be calculated from the depression of the freezing point in solutions of cuprous oxide and cuprous sulphide in copper, observed by Heyn (*loc. cit.*) and Heyn and Bauer (*Metallurgie*, 1906, **3**, 73). They showed that these form no solid solutions with copper, and give a normal lowering. The following table gives the data and the calculated values of E .

TABLE I.

Cuprous oxide, per cent.	Depression (t) in degrees.	Concentration (m) in gram-molecule per 100 grams of copper.	E (from $t = Em$).
1.16	7.5	0.00820	914
1.75	13.5	0.01244	1082
3.45 (eutectic)	18.5	0.0250	740
3.45	19.2 *	0.0250	768
3.45	20 †	0.0250	800
0.98	6	0.00621	967
1.88	10	0.01204	830
2.92	13	0.01890	688
3.82 (eutectic)	18	0.02496	722

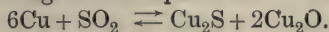
* From Holborn and Day's measurement (*Ann. Physik*, 1900, [iv], **2**, 505).

† From author's result for eutectic, see Expt. 4(d).

The table shows the uncertainty of E due to the uncertainty of Heyn and Bauer's measurements of t . The value of t given by Holborn and Day for the eutectic solution of cuprous oxide in copper is probably fairly correct. The value of E shows a general decrease with increasing concentration. On all considerations the author has used the formula $E = 845 - 6(t - 10)$, where t = depression in degrees, as best representing the available facts, theoretical and otherwise, for depressions of 10° and over.

Using this value of E , it was at once clear from the first experi-

ment that the depression of freezing point by sulphur dioxide was more than double, but not treble, that which would take place did the gas dissolve in copper as simple molecules. (The significance of the depression will be more accurately calculated later.) This fact, taken in conjunction with the constancy of \sqrt{p}/m shown by Sieverts and Krumbhaar, appeared to point to an actual dissociation of the sulphur dioxide in solution. It is difficult to imagine this on any other hypothesis than the formation of cuprous oxide and sulphide, according to the equation:



If the formation of oxide and sulphide were practically complete, this would give three times the depression calculated for sulphur dioxide, and would make $\sqrt[3]{p}$ instead of \sqrt{p} proportional to m . The former result would be in disagreement with the author's, and the latter with that of Sieverts and Krumbhaar, this being the chief difficulty expressed in the recent paper of Sieverts and Bergner (*loc. cit.*) in the way of a simple chemical explanation of the facts. The difficulty is removed if the above reaction is supposed to be only partly complete. This may be shown as follows: Let m be the molar concentration of total sulphur dioxide apparently dissolved by the copper, and of this let a fraction x go to form cuprous sulphide and cuprous oxide, so that the actual concentrations of sulphur dioxide, cuprous sulphide, and cuprous oxide will be $m(1-x)$, mx , and $2mx$ respectively. Then for equilibrium, supposing the solution dilute, so that the concentration of copper may be regarded as constant,

$$km(1-x) = 4m^3x^3 \quad (1).$$

If the sulphur dioxide dissolved as such obeys Henry's law,

$$m(1-x) = k'p \quad (2),$$

where p is the pressure of gas in equilibrium with the solution. By eliminating x , we obtain:

$$m = k'p + \sqrt[3]{\frac{kk'p}{4}} \quad (3).$$

If now the constants k and k' are such that when $p = p_A$ (atmospheric pressure), $m = m_A$ and $x = x_A$, from equation (1),

$$km_A(1-x_A) = 4m_A^3x_A^3 \quad (4),$$

and from equation (2),

$$m_A(1-x_A) = k'p_A \quad (5).$$

Hence, substituting for k and k' in equation (3),

$$\frac{m}{m_A} = (1-x_A) \frac{p}{p_A} + x_A^3 \sqrt[3]{\frac{p}{p_A}} \quad (6).$$

An equation of this form was deduced by Sieverts and Bergner for the case of partial formation of oxide and sulphide, and apparently assumed by them to be quite inconsistent with the observed proportionality of \sqrt{p} and m . This would undoubtedly be so in general, but over the range of pressures examined by Sieverts and Krumbhaar it may be shown that for a certain value of x_A such proportionality would approximately hold between \sqrt{p} and m as calculated from equation (6). The following table gives for the actual pressures used in their experiment at 1123° by Sieverts and Krumbhaar the values of \sqrt{p}/m calculated from equation (6), taking $p_A=1$ and $m_A=1$, and assuming different values for x_A . The last two lines represent respectively the values of \sqrt{p}/m given by Sieverts and Krumbhaar in their own units, and what these values would be in terms of the units taken above (atmospheric pressure, and concentration at atmospheric pressure).

TABLE II.

Pressure in mm. of mercury.	999.	760.	729.	513.	322.	115.	54.
\sqrt{p}/m (calc.) for $x_A=0.25$	0.911	1	1.015	1.132	1.289	1.578	1.701
$x_A=0.5$	0.952	1	1.008	1.059	1.109	1.138	1.009
$x_A=0.6$	0.970	1	1.004	1.031	1.050	1.022	0.963
$x_A=0.65$	0.979	1	1.002	1.019	1.022	0.975	0.906
$x_A=0.7$	0.988	1	1.001	1.006	0.998	0.930	0.857
$x_A=0.75$	0.998	1	0.999	0.994	0.973	0.889	0.812
$x_A=0.8$	1.007	1	0.998	0.981	0.949	0.852	0.772
\sqrt{p}/m (experimental, Sieverts and Krumbhaar)	$\left\{ \begin{array}{l} 61.0 \\ 1.001 \end{array} \right.$		60.8	60.7	60.7	58.3	56.1 (?) *
		1	0.999	0.998	0.996	0.958	(?)

* There appears to be some error in arriving at this value from the data.

The above table is calculated on the assumption that the solution of sulphur dioxide in copper is a very dilute one. A rough calculation, which space does not allow to be given here, showed that the decrease of concentration of the copper (owing to formation of cuprous sulphide and cuprous oxide), which concentration would appear as a sixth power in the equilibrium equation, might raise the calculated values of \sqrt{p}/m by some $2\frac{1}{2}$ per cent. at the highest pressure, and by less as the pressure is lowered. Taking this into consideration, inspection of the table shows that $x_A=0.7$ gives the best, and, on the whole, considering experimental errors, a very satisfactory agreement between calculated values of \sqrt{p}/m and those observed by Sieverts and Krumbhaar. Their results may thus be explained by supposing that at the various temperatures they employed, and at atmospheric pressure, about 0.7 of the dissolved sulphur dioxide reacted to form cuprous sulphide and cuprous oxide, the remainder being dissolved as simple gas molecules. At lower pressures, as may be seen from equations (1)

and (2) above, by eliminating m , the proportion of sulphur dioxide transformed will be greater, at higher pressures less.

In the author's experiments a little oxidation of the copper usually took place between the passing of hydrogen and of sulphur dioxide. It remains to be seen what influence this would have on the depression caused by the latter, on the above hypothesis of chemical equilibrium. If a concentration a of cuprous oxide is present before sulphur dioxide is passed, and y is the total concentration of cuprous oxide after saturating with the gas at atmospheric pressure, $\frac{y-a}{2}$ will be the concentration of cuprous sulphide formed; and hence for equilibrium:

$$\begin{aligned}\frac{y-a}{2} \cdot y^2 &= k k' p_A \text{ (from equations (1) and (2) above)} \\ &= 4m_A^3 x_A^3 \text{ (from equations (3) and (4)),}\end{aligned}$$

or

$$y^3 - ay^2 = 8m_A^3 x_A^3 \quad \dots \quad (7).$$

As m_A and x_A are known, the solution of this cubic equation gives y . If a is relatively small, so that squares and higher powers are negligible, it follows from equation (7) that

$$y - a/3 = 2m_A x_A.$$

Hence the total molar concentration of sulphur dioxide, cuprous oxide, and cuprous sulphide is $m_A(1 - x_A) + \frac{y-a}{2} + y$, that is, $m_A(1 + 2x_A)$, the same molar concentration as in a solution of sulphur dioxide in pure copper; thus small concentrations of cuprous oxide do not affect the total depression caused by sulphur dioxide.

Using this result, the true depression caused by sulphur dioxide at atmospheric pressure is given by experiments 1, 2, and 3 as 169.5, 170.5, and 180.5 microvolts, that is, 13.05°, 13.15°, and 13.9° respectively. Giving only half weight to the first value, as the freezing point in hydrogen was in that case less certain, the mean value for the depression is 13.43°; this corresponds with a concentration of $\frac{13.43}{824} = 0.0163$ gram-molecule per 100 grams of copper. By extrapolation from Sieverts and Krumbhaar's results, however, the solubility at 1083° - 13° = 1070° is 0.412 gram or $\frac{0.412}{64.07} = 0.00644$ gram-molecule of sulphur dioxide per 100 grams of copper; thus, according to depression measurements there are $\frac{0.0163}{0.00644} = 2.54$ times as many molecules dissolved as would correspond with the simple formula SO_2 . If 0.7 of the sulphur dioxide

had passed into oxide and sulphide, the number of dissolved molecules would, from the equilibrium chemical equation, be multiplied by $1 + 2x_A$, that is, $(1 + 2 \times 0.7) = 2.4$. Considering the sources of error in the value taken for the constant E (see above), in the measurement of the freezing-point depression, in Sieverts and Krumphaar's measurement of solubility and extrapolation of the same over 50° , etc., the agreement between this result deduced from independent theoretical considerations, and the former value 2.54 obtained by depression measurements, is satisfactory and noteworthy.

In order to test and confirm the view, supported by both the above lines of reasoning, that the sulphur dioxide dissolved in molten copper consists only partly of the unchanged molecules (about 0.7 at atmospheric pressure reacting to form sulphide and oxide), experiments 3 (*e* and *f*) and 4 were performed, in order to examine the influence of excess of cuprous sulphide or cuprous oxide respectively on the depression caused by sulphur dioxide. In 3(*e*) cuprous sulphide was formed in an amount estimable by the depression it caused. If b is this molar concentration of cuprous sulphide, and z is the amount of cuprous oxide formed when sulphur dioxide is now passed, it may easily be shown that an equation analogous to equation (7) holds, namely:

$$z^3 + 2bz^2 = 8m_A^3 x_A^3 \quad \dots \dots \dots (8).$$

b is found from the formula $t = Em$ to be 0.0128 gram-molecule per 100 grams of copper; m is, as shown above, 0.00644 . Hence:

$$z^3 + 0.0256z^2 = 8 \times (0.00644)^3 x_A^3.$$

If $x_A = 0.7$, this equation gives $z = 0.00490$.

Hence the total molecular concentration, due to the original cuprous sulphide, the cuprous sulphide and cuprous oxide formed by the sulphur dioxide, and the unchanged sulphur dioxide, is $0.0128 + (\frac{3}{2} \times 0.00490) + (0.3 \times 0.00644) = 0.0221$ gram-molecule per 100 grams of copper. This would give a depression of 17.65° , or 6.9° over that due to the original cuprous sulphide alone. If $x_A = 1$ (that is, if the action of the sulphur dioxide on the copper were complete), it may similarly be shown that 19.45° , or 8.7° extra, depression would be caused. The actually observed depression, from experiment 3(*f*), was 16.25° , or 5.5° extra. This result agrees much better with that calculated for $x_A = 0.7$ than for $x_A = 1$; it also shows how, in accord with the theory, the addition of one of the products of reaction has strikingly diminished the solubility of sulphur dioxide, the depression in this case diminishing from 13.45° to 5.5° .

In experiment 4, similar measurements were made of the influence of the presence of cuprous oxide on the depression due

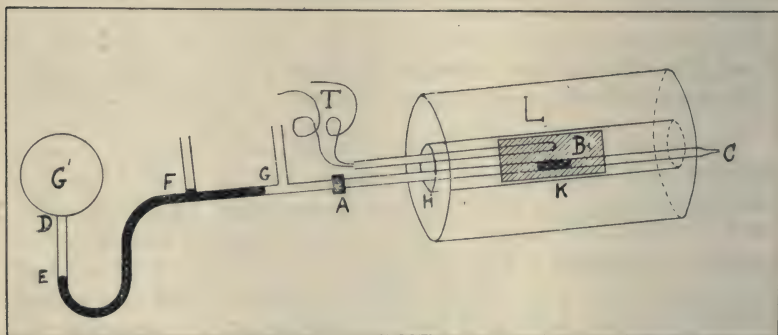
to sulphur dioxide; this was done for a concentration of cuprous oxide less than, and for one equal to, the eutectic concentration. The values of the depressions in the former case are indicated by the first halt-points in experiments 4 (*d*) and (*e*), those in the latter case by the second constant halt. The calculations of the results are similar to the one just given (a modification in the case of the eutectic point being, of course, that here the concentration of cuprous oxide was constant), and need not be given at length. In the case of the lower concentration of cuprous oxide, the calculated extra depression would be 3.45° if $x_A = 0.7$, 4.5° if $x_A = 1$. The value 3.75° or 4.75° (the latter from the value marked "doubtful" in the experiment) was actually observed. In the case of the eutectic concentration, the calculated extra depression would be 1.75° if $x_A = 0.7$, 1.3° if $x_A = 1$; actually observed, 2.1° . The tendency of these supplementary experiments is seen to be to confirm the hypothesis of a partial combination of the sulphur dioxide dissolved in molten copper.

PART II.—*Equilibrium between Sulphur Dioxide, Solid Copper, Cuprous Sulphide, and Cuprous Oxide at High Temperatures.*

The relation between sulphur dioxide, solid copper, cuprous sulphide, and cuprous oxide at temperatures up to 730° has been recently examined by Schenck and Hempelmann (*Metall. u. Erz.*, 1913, 1, 283), and shown to be a most interesting case of heterogeneous equilibrium. The equation is $6\text{Cu} + \text{SO}_2 \rightleftharpoons \text{Cu}_2\text{S} + 2\text{Cu}_2\text{O}$. There are three solid phases and one gaseous, and three components, so that, according to the phase rule, the system should be univariant. This was found to be so, at each temperature there being a definite pressure of sulphur dioxide in equilibrium with the solids. This equilibrium pressure reaches atmospheric at 730° , and is then increasing rapidly with temperature. It was of interest in connexion with the present work to extend the measurements to much higher temperatures, if possible to the melting point of the mixture of solids. This has been done by means of the apparatus represented in Fig. 1. *AC* was a thick-walled tube of fused silica, of 5 mm. internal diameter, drawn off to a capillary at *C*; this fitted through a hole bored in the graphite block *B*, placed in the electrical resistance furnace *L*. Into a second hole in the graphite fitted the thermo-couple *T*. The graphite ensured evenness of temperature in the middle of the furnace. The reaction mixture occupied about 5 cm. of the length of the silica tube, at *K*, which, with the thermo-junction, was situated at the centre of the furnace. The latter could, by

an external regulating resistance, easily be kept constant at any desired temperature to within 1° . The ends of the furnace were closed by suitable non-conducting diaphragms. After placing the charge in the tube AC , the end A was cemented by Golaz wax to the glass tube AED , which was similarly cemented at D to the hydraulic gauge G' . The gauge and the portion of tube DE were filled with water; from E towards A the tube contained mercury. At F and G two side-tubes were sealed on to the tube AE . The charge K was originally finely divided copper, prepared by reducing cupric oxide in hydrogen. This was converted into a mixture of copper, cuprous oxide, and cuprous sulphide by passing dried sulphur dioxide in at C , through the copper, and out of the side-tube G , the mercury during this part of the experiment being between F and G ; during the passing of sulphur dioxide, which lasted about forty-five minutes, the temperature was kept

FIG. 1.



at about 700° , at which temperature, according to Schenck and Hempelmann, the equilibrium pressure is considerably below atmospheric, and reaction fairly rapid. That the copper was not completely converted into oxide and sulphide was shown by the fact that, on sealing the apparatus, the pressure decreased to below atmospheric, indicating further absorption. While the gas was still passing, the tube G was sealed off. Mercury was then admitted through F until the mercury column reached H . The tube F , and finally the capillary C , were then sealed off, the latter in the oxy-coal gas flame. The reaction mixture was thus in an atmosphere of sulphur dioxide, and it only remained to heat the furnace to various temperatures, and read the pressures recorded. An advantage of the apparatus, which worked very successfully, was that the volume of gas was practically constant, thus enabling a smaller amount of the reacting materials to be used, and

ensuring a rapid coming to equilibrium. At each definite temperature the pressure became steady in ten minutes, and gave the same value with rising or falling temperatures. The purpose of passing the mercury along the tube to *H* was as follows. At the pressures investigated, sulphur dioxide would liquefy at the ordinary temperature, whilst if the seal *A* were raised in temperature the Golaz wax would soften. By the device adopted, the heat from the furnace kept the mercury at *H* hot enough to avoid liquefaction of sulphur dioxide, and the cement at *A* was kept cool by a stream of water. The gauge *G'* was calibrated against a mercury column, and indicated pressures to within 1 cm. of mercury.

The apparatus as described is that used in the finally successful and satisfactory experiment. In a former experiment, the results of which, so far as they go, are confirmatory of those of the second, a modification was employed which it may be of interest to mention. The tube *DEAC* here consisted of hard glass throughout, thus avoiding the wax seal at *A*, and allowing the tube *F* to be dispensed with, the part of the tube outside the furnace being simply kept warm down to the mercury by an electric heating coil. The part of the tube within the furnace was encased in a closely-fitting iron tube, which fitted into the graphite block. This device acted perfectly in withstanding pressure, the glass wall being simply blown out against the iron tube, and no leak occurring even under several atmospheres. Up to 1000° all went well, but on attempting to heat higher, the glass apparently became so soft that it flowed and blocked the tube, bringing the experiment to an end. Still, this simple device could doubtless be safely used for high pressure work at lower temperatures.

The following table gives the equilibrium pressures of sulphur dioxide at various temperatures. The bracketed values are taken from Schenck and Hempelmann's results, and show good continuity with the author's. The values for experiment I, with the glass tube, are given for purposes of comparison; they are lower than those in experiment II, this being in all probability due to the large conduction of heat along the iron tube to its cool ends, causing the temperature to be lower than that registered by the thermo-couple (iron being a much better conductor than graphite). A less sensitive gauge was also used in experiment I, as higher pressures were expected.

TABLE III.

Temperature.	Pressure (in cm. of mercury) of sulphur dioxide in equilibrium with solid copper, cuprous sulphide, and cuprous oxide.	
	I. Expt. in glass tube.	II. Expt. in silica tube.
614°	—	(16·6)
662	—	(33·2)
722	—	(67·8)
730	—	(76·5)
726·5	48·5	69·0
768	90·5	110·3
810·5	141·0	164·9
851·5	209·0	230·4
893	278·5	305·2
931·5	341·0	377·0
973·5	391·5	435·5
1012·5	—	476·5
1051·5	—	491·0 (?)

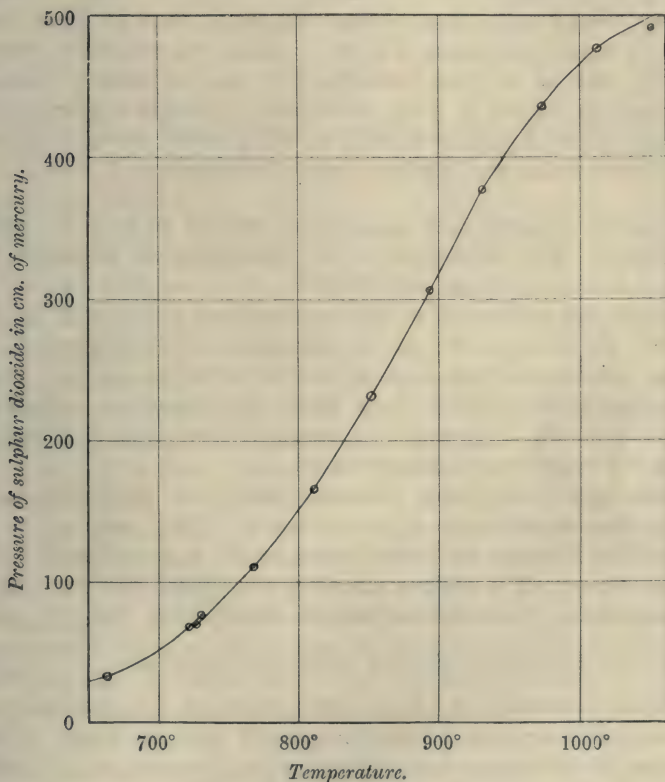
On heating above 1050° (at about which temperature the mixture would begin to melt), the pressure suddenly began to go down, perhaps owing to the cuprous oxide in the fusion attacking the silica.

The values obtained in experiment II are taken as correct, and are shown graphically by the curve in Fig. 2. The lower curve is Schenck and Hempelmann's.

There is an interesting point of connexion between the equilibrium between sulphur dioxide and copper, cuprous oxide and cuprous sulphide in solution, discussed in part I of this paper, and the equilibrium between sulphur dioxide and the solid substances investigated above. At a definite temperature it will be possible for sulphur dioxide, solid copper, solid cuprous oxide, solid cuprous sulphide, and solution to exist together, there being now five phases, three components, and consequently a non-variant system. This temperature is, of course, that at which a eutectic mixture of cuprous oxide, cuprous sulphide, and copper would be on the point of crystallising out. If it could be assumed that cuprous oxide and cuprous sulphide would not affect each other's solubility in copper, the temperature and composition of the solution at this point could be calculated by extrapolation of Heyn's (*Zeitsch. anorg. Chem.*, 1904, **39**, 1) and Heyn and Bauer's (*Metallurgie*, 1906, **3**, 73) solubility curves for cuprous oxide and cuprous sulphide respectively, and from the value of the freezing-point depression constant. The author has attempted to make a rough calculation on these lines, the result of which would set the temperature at 1055°, the molar concentrations of cuprous oxide and cuprous sulphide per 100 grams of copper in the saturated solution being 0·0221 and 0·0159 respectively. The

product $[\text{Cu}_2\text{S}][\text{Cu}_2\text{O}]^2$ is therefore $\frac{0.0159 \times 0.0221^2}{4m_A^3 x_A^3}$ times that at atmospheric pressure, where m_A = solubility of sulphur dioxide in copper at atmospheric pressure and 1055° , x_A the fraction of it which combines with the metal. If Henry's law holds for the part of the sulphur dioxide in simple physical solution, the equilibrium pressure in the non-variant system must therefore be

FIG. 2.



$\frac{0.0159 \times 0.0221^2}{4m_A^3 x_A^3}$ atmospheres. By extrapolation from Sieverts and Krumbhaar's values, m_A is found to be about 0.00632 gram-molecule per 100 grams of copper. Hence, if x_A (as shown to be probable in part I of this paper) is about 0.7, the equilibrium pressure should be 22.4 atmospheres. If, on the other hand, $x_A = 1$, it would be 6.5 atmospheres. The equilibrium pressure at 1055° over a mixture of copper, cuprous sulphide, and cuprous oxide is,

however, known approximately from the results tabulated above; it lies between 6.5 and 7 atmospheres. The striking agreement of this result with that calculated above for $x_A = 1$ might appear at first to contradict the conclusion reached in the first part of the paper, that x_A is about 0.7. Reflection, however, suggests that the agreement may be only accidental, for the assumption made above that cuprous sulphide and cuprous oxide, both in considerable concentration, do not influence each other's solubility is certainly not tenable, and a reduction of 30 per cent. in their solubility would more than reduce the high value of 22.4 atmospheres to the experimental 6.5 or 7. Also, the solubility curves, especially that of cuprous sulphide, are not accurately enough determined to admit of even moderately accurate extrapolation. The effect of the change of solvent on the physical solubility of the sulphur dioxide has also not been taken into account.

The results obtained and conclusions arrived at may be briefly recapitulated. The depression of the freezing point of copper by dissolved sulphur dioxide was found to be about 2.54 times that expected if the molecules of the gas existed unchanged in the solution. This was shown to be explicable on the hypothesis of a partial reaction of the sulphur dioxide with the copper. Complete reaction would give three times the depression calculated from the formula SO_2 , and the amount of gas dissolved should vary as the cube root of the pressure.

Sieverts and Krumbhaar, however, found the concentration to vary as the square root of the pressure. The assumption of Sieverts and Bergner that the latter result is incompatible also with the theory of a partial reaction was shown not to hold if the reaction in the solution under atmospheric pressure were about 70 per cent. complete, the calculated values of $\frac{\sqrt{\text{pressure}}}{\text{concentration}}$ under these conditions showing good agreement with Sieverts and Krumbhaar's "constant." Such a partial reaction would give a depression of 2.4 times that calculated for the formula SO_2 , thus agreeing satisfactorily with the author's determined value. Supplementary experiments on the influence of excess of cuprous sulphide or oxide on the depression caused by sulphur dioxide supported these views. The equilibrium pressures of sulphur dioxide in the univariant system copper, cuprous oxide, cuprous sulphide (all solid), and sulphur dioxide have also been measured between 700° and 1050° , the pressure rising from less than 1 to 7 atmospheres. The high value at the latter temperature explains the "insolubility" of sulphur dioxide in solid copper at high

temperatures and ordinary pressures, noted by Sieverts and Krumbhaar.

In conclusion, the author desires to acknowledge his indebtedness to Prof. F. G. Donnan for his invaluable advice and suggestions.

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CLVI.—*The Molecular Condition of Mixed Liquids.*
Part I. Mixtures of the Lower Aliphatic Alcohols
with Water.

By WILLIAM RINGROSE GELSTON ATKINS and THOMAS ARTHUR
WALLACE.

WHILE engaged in measurements of the densities of mixtures of allyl alcohol and water, the old problem of the relation of solvent and solute obtruded itself forcibly on our attention. In spite of the number of investigators who have attacked this question, the subject can hardly be regarded as exhausted. The results given below are the first of a series which the authors hope to complete.

At the outset it seemed possible that freezing-point determinations of solutions of the alcohols and water in some suitable solvent might give indications of the formation of hydrates, especially in a solvent of low freezing point. That such hydrates do not exist at high temperatures has been shown by Ramsay and Young (P., 1888, **4**, 101), also by Young and Fortey (T., 1902, **81**, 724), and the abnormally high vapour pressures of mixtures of alcohol and water as determined by Konowaloff (*Ann. Phys. Chem.*, 1881, [iii], **14**, 34) show clearly that the attraction of the alcohol molecules for one another must be greater than that of the alcohol for water molecules, which accordingly yield mixtures of minimum boiling point constant in composition.

On the other hand, it has been demonstrated by Paternò and Ampola (*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 153) that trimethylcarbinol does form a hydrate, $(\text{CH}_3)_3\text{C}\cdot\text{OH}\cdot 2\text{H}_2\text{O}$, melting at 0° , and largely dissociated in solution. The freezing-point-composition diagram, density, and viscosity determinations all point to its existence at temperatures below 29.4° .

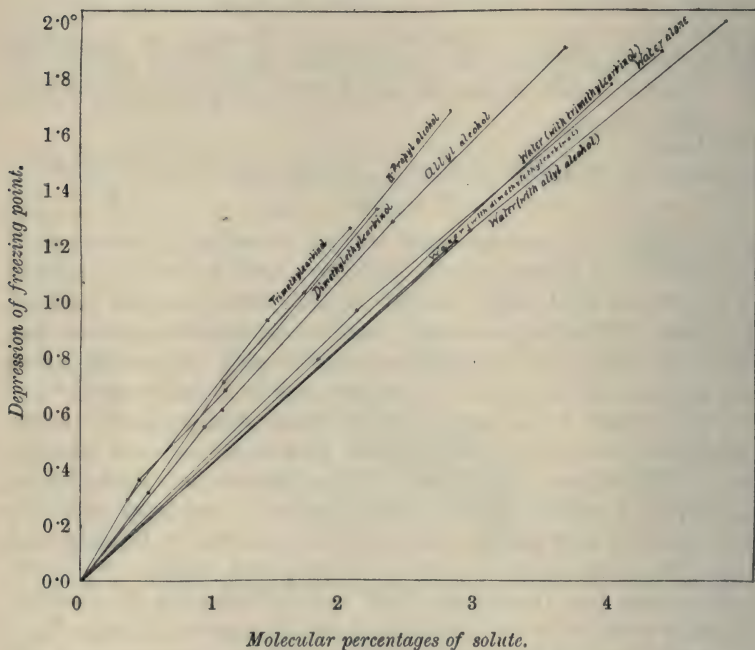
It may here be noted that there is no connexion between the

minimum boiling-point mixture, which contains 88.24 per cent. of alcohol (S. Young, "Fractional Distillation," p. 233), and the above-mentioned hydrate, in which 67.14 per cent. is found.

The possession by this alcohol of the most highly branched form of carbon chain and of the greatest possible degree of molecular mass symmetry combine to raise its melting point; accordingly it is possible to investigate its freezing-point-composition diagram with water very readily; with phenol it has been proved, by

FIG. 1.

Molecular depressions of freezing point of alcohols and water in aniline.



similar methods, to form two compounds (Paternò and Mieli, *loc. cit.*, 1908, [v], 17, i, 396). The low freezing points of the other alcohols and the viscous character of the liquids before solidification render their investigation by the above method very difficult, if not impossible.

Now, since a complex alcohol, such as trimethylcarbinol, forms a hydrate at low temperatures and gives an abnormal vapour pressure curve with water, at any rate at high temperatures, it seems probable that the formation of hydrates may also take place

in the case of the lower alcohols, which are much more closely related to water.

Accordingly, measurements were made of the depression of the freezing point of aniline occasioned by the addition of (1) water, (2) the alcohols singly, and (3) mixtures of the two classes of substances. The numerical results are given in the experimental portion of the paper, but Fig. 1 shows the molecular concentration-freezing point diagram. In no case was decided evidence obtained in favour of the combination of an alcohol with water, as shown by the closeness of the curves for water alone and with alcohols. This, of course, is not a proof that such combinations do not exist, for no indication was found of the presence of the trimethylcarbinol hydrate before mentioned. The curve for water in the presence of *n*-propyl alcohol is omitted for clearness, as it lies between the lower portions of those for water alone and in presence of trimethylcarbinol. Evidently the aniline dissociates such molecular complexes almost completely, as might be expected from its distinctly basic character. In the case of allyl alcohol and of dimethylethylcarbinol, the somewhat unusually low values found for the depression of freezing point by the subsequent addition of water indicate the existence of hydrates in these cases, but as the variations are not large, it is possible that they may not be outside the range of experimental error. Inspection of Fig. 1 shows the order of the association of the dissolved substances. Thus, whilst water gives a molecular weight of 22 to 24 instead of 18, allyl alcohol is found to vary from 60 to 66 (Calc., M.W.=58), and *n*-propyl alcohol from 58 to 59 (Calc., M.W.=60). Turning now to trimethylcarbinol, the figures are from 54 to 72 with increasing concentration (Calc., M.W.=74), whilst dimethylethylcarbinol rises from 63 to 88 (Calc., M.W.=88). It appears therefore as if these substances were dissociated in solution, a very unlikely occurrence. The true explanation of the abnormality appears to be that aniline does not at once give out all its latent heat of solidification, as shown by de Forcrand (*Compt. rend.*, 1903, **136**, 945), this being due to the separation of an unstable crystalline modification. The behaviour of trimethylcarbinol as a cryoscopic solvent (Atkins, T., 1911, **99**, 10) is quite similar, but more marked, although in this case, owing to the rapid transformation* of the unstable into the stable modification de Forcrand did not suspect the existence of the former. From a consideration of the equations concerned, it is clear that a low value for the heat of solidification will give a correspondingly low value for the molecular weight of any solute.

* Experiments, at present in progress, show the existence of the unstable modification by a study of the volume changes after solidification.

Thus all the above molecular weights must be too low, that is, the association of the solutes appears to be less than it really is.

An attempt was made to use benzene as a solvent for a similar series of determinations, but it was found that the solubility of water in the alcoholic benzene was so small that it occasioned a rise in the freezing point of the solvent, by extracting some of the dissolved alcohol. Use was made of this phenomenon to determine the partition-coefficient of allyl alcohol between benzene and water. The ratio C_w/C_b was found to fall from 14.3 to 7.5 as the concentration increased. This point is further considered in the experimental portion of the paper. Values for the molecular weight of the alcohol in benzene rose from 65 to 109 with increasing concentration (Calc., M.W.=58).

In view of the failure of the cryoscopic method to give any decided evidence on the problem, determinations were made of the densities of equimolecular mixtures of various alcohols and water at a series of temperatures and also of the pure alcohols over the same range. From the figures so obtained, it was possible to calculate the contractions in volume on mixing the alcohols and water at different temperatures. In Fig. 2 the straight or slightly curved lines are shown which represent the changes in density with temperature. Table I records, for various temperatures, the volume of a gram calculated and found, the percentage contraction, and the weight percentage of alcohol in each mixture, together with that required for equimolecular proportions. The densities and boiling points of the pure alcohols employed are given in the experimental part.

TABLE I.

Mixtures of Alcohols and Water.

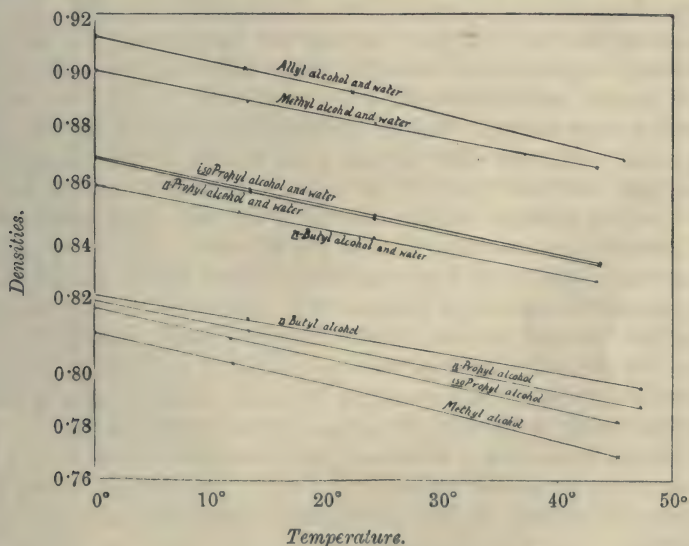
	Alcohol, per cent.		t° .	Vol. of a gram calc.	Vol. of a gram found.	Con- traction, per cent.
	Actual.	Theory.				
Methyl alcohol ...	64.18	64.00	0	1.1504	1.1107	3.416
	64.18	64.00	43.4	1.1953	1.1531	3.530
<i>n</i> -Propyl alcohol ...	77.44	76.92	0	1.1685	1.1494	1.634
	77.44	76.92	43.7	1.2106	1.1981	1.032
<i>iso</i> Propyl alcohol...	77.17	76.92	0	1.1709	1.1485	1.913
	77.17	76.92	43.7	1.2187	1.1999	1.543
Allyl alcohol	76.60	76.32	0	1.1142	1.0962	1.615
	76.60	76.32	45.7	1.1593	1.1496	0.837
<i>n</i> -Butyl alcohol ...	80.95	80.43	0	1.1730	1.1608	1.040
	80.95	80.43	43.4	1.2119	1.2072	0.388

The above results show that the contraction on mixing decreases as the molecular weight of the alcohol increases, with the exception

of the case of allyl alcohol at 0° , which shows a slightly smaller contraction than does *n*-propyl or *isopropyl* alcohol. It is remarkable how closely allyl and *n*-propyl alcohols resemble one another in this respect, and in their behaviour on distillation (Wallace and Atkins, T., 1912, 101, 1959). Again, the *iso*-alcohol gives a greater contraction than does the normal. It was not possible to study the behaviour of *isobutyl* alcohol, as it is not miscible with water in equimolecular proportions. The contractions and the association factors, as determined by Ramsay and Shields, diminish in the same order.

FIG. 2.

Densities of pure alcohols and of equimolecular mixtures of alcohols and water.



With regard to the influence of temperature on the contraction, it is to be expected, in accordance with the theorem of Le Chatelier, that as heat is given out on mixing, an increase in the temperature at which the mixture is made will be accompanied by a smaller heat evolution, and accordingly by a smaller contraction. The change in heat evolution with rise in temperature has been studied exhaustively by E. Bose (*K. Ges. Wiss. Göttingen Nachr. Math.-Phys.*, 1906, p. 309). It has, however, been pointed out by Young ("Fractional Distillation," p. 32) that the two phenomena do not always proceed *pari passu*. The foregoing expectation is realised in every case except that of methyl alcohol,

where an increase in contraction is observed at the higher temperature.

In Fig. 2 are shown the variations in density of the pure alcohols and of their equimolecular mixtures with water, occasioned by rise in temperature. It is clear in the diagram that the change of density with temperature is greatest in the alcohol which has the largest association factor, and that the other alcohols follow in order of decreasing association. In other words, the expansion of a liquid is really due to two effects at least, one the larger volume occupied by each molecule, and the other the larger number present owing to the breaking up of associated molecules. Thus the more highly associated a liquid is, the greater will be its coefficient of expansion, at any rate for substances of the same type. Turning now to the equimolecular mixtures in Fig. 2, it will be noticed that they all slope towards the temperature axis at much the same angle and are straight lines, with the exception of the allyl alcohol mixture, which gives a slightly curved line at the higher temperatures. Whilst, however, the slope of the mixtures is greater than the slope of the pure liquids in the majority of cases, the two are equal in the case of *isopropyl* alcohol, and in the case of methyl alcohol the slope of the pure substance is considerably greater than that of the mixture. The pure alcohol, it may be noted, shows slight curvature at the higher temperatures. The above facts seem to indicate that association in the mixtures is greater than in the pure alcohols for the higher members of the series, equal in the case of *isopropyl* alcohol, and less in the case of methyl alcohol. This reasoning does not, however, show whether the association is due to formation of complexes among the like or unlike molecules. However, the similarity of slope for the mixtures, as compared with that for the pure alcohols, gives some evidence in favour of the association being between the unlike molecules. On the supposition that this view is correct, an explanation can be given of the behaviour of methyl alcohol. Employing the values given by Ramsay and Shields (T., 1893, 63, 1102) for the association factors of the alcohols over the range 16–46°, $x=3.43$ for methyl, 2.25 for *n*-propyl, 2.86 for *isopropyl*, 1.88 for allyl, and 1.94 for *n*-butyl alcohols.

It is evident that of the above values of x only that for methyl alcohol is much higher than two. Now, assuming that one molecule of water becomes associated with one molecule of an alcohol, the average association of the liquid will be $x=2$. Accordingly, the slope of the density-temperature lines will be much the same in the case of the pure alcohols, for which $x=2$, and in the mixtures. Reference to Fig. 2 shows that this is so. In the case of methyl

alcohol, however, the high association factor of the pure liquid is greatly lowered in the equimolecular aqueous mixture; accordingly, as may be seen from Fig. 2, the slope of the line representing the behaviour of the pure alcohol is much greater than that of the mixture; there is therefore an increase in the contraction in volume as the temperature rises. This will evidently be the case as long as the association of the pure alcohol is greater than that of the mixture, but after such a condition ceases to hold good it is to be expected that methyl alcohol will behave like the others. This point is being tested by further work.

Information as to the molecular condition of the mixtures was also sought by employing Traube's atomic volumes to calculate their molecular volumes, first on the assumption that they were mixtures, and secondly, on the assumption that they were equimolecular compounds, or associated as double molecules. This method had previously been tested by one of us (Atkins, P., 1910, **26**, 337) for binary mixtures of organic substances, for some of which independent evidence existed that compounds were formed.

Thus it was found that whilst *o*-nitrophenol and *p*-toluidine form no compound, the opposite is the case with phenol and α -naphthylamine, phenol and *p*-toluidine, phenol and carbamide, aniline and *p*-cresol, *p*-toluidine and α -naphthol. The evidence obtained by Traube's method agrees in the above cases with that furnished by Philip (T., 1903, **83**, 814) from a study of the freezing-point diagrams and by Treitschke's viscosity measurements (*Zeitsch. physikal. Chem.*, 1907, **58**, 425). In the case of thiocarbamide and ammonium thiocyanate, the presence of a compound is also indicated by this method, in accord with the results of the freezing-point diagram (Atkins and Werner, T., 1912, **101**, 1167). Fused chloral hydrate is also shown to be a compound, as is well established from its magnetic rotation and by purely chemical evidence. In the single instance of phenol and diphenylamine, Traube's method points to the existence of a compound, whereas Philip has shown that no such compound exists. Here, however, it is quite probable that the association is between the diphenylamine molecules, and to a less extent between the phenol molecules, like with like. The above results are such as to justify the employment of Traube's values in the calculation of molecular volumes of mixed liquids, the more so when it is remembered that the densities of the liquids were measured at high temperatures, 105° in one case, and that the co-volume had to be corrected for temperature by employing as a hypothetical value the equation $v_t = v_0(1 + \alpha t)$, where α is the coefficient of expansion of a gas.

Table II shows the results obtained with the mixtures of alcohol

and water. The association factor for the pure alcohol is also given as determined by the same method. The exact composition of the very closely equimolecular mixtures is given in table I.

TABLE II.

Molecular Volumes of Alcohols and of their Equimolecular Mixtures with Water.

Liquid.	<i>t</i> °.	Mixtures.			Pure liquid.		
		<i>V</i> calc. as mixture.	<i>V</i> calc. as com-pound.	<i>V</i> found.	<i>V</i> calc.	<i>V</i> found.	Assoc. of pure liquid.
		c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Water	0°	—	—	—	33·0	18·0	1·83
Methyl alcohol	0	82·1	57·6	44·1	49·1	39·5	1·24
	43·4	89·9	61·5	57·6	53·0	41·6	1·22
<i>n</i> -Propyl alcohol ...	0	114·3	89·8	89·7	81·3	73·1	1·11
	43·7	122·1	93·7	94·2	85·2	76·1	1·12
Allyl alcohol	0	106·4	{ 81·9 83·6* 86·0 87·7* }	83·3	75·1	66·6	1·13
	45·7	114·6		87·4	79·2	69·9	1·13
<i>iso</i> Propyl alcohol ...	0	114·3	89·8	89·6	81·3	73·3	1·11
	43·7	122·1	93·7	93·6	85·2	76·8	1·11
<i>n</i> -Butyl alcohol	0	130·4	105·9	106·9	97·4	89·8	1·08
	43·4	138·2	109·8	111·2	101·3	93·2	1·08

* In these two cases, Traube's negative value for the double bond was not subtracted.

Inspection of the figures in the table shows a remarkably close agreement between the molecular volumes found and those calculated on the assumption that compounds exist. In the case of methyl alcohol and water, the molecules of the compound are even further associated among themselves. It is noteworthy that with allyl alcohol the value found, omitting the double bond in the calculation, is in better agreement with the result of experiment. That the bond is not actually destroyed is obvious from the behaviour of the mixture to bromine, also the corresponding double hydroxy-compound is known.

The foregoing explanation of the behaviour of the alcohols and water on mixing is diametrically opposed to that given by Holmes (T., 1906, 89, 1774) and later by Holmes and Sageman (T., 1907, 91, 1606) for the behaviour of certain salts. These authors deny the formation of hydrates in solution both by organic liquids and by salts.

EXPERIMENTAL.

The liquids employed were distilled through a five- or three-section Young evaporator still-head. The freshly distilled products

were used for cryoscopic experiments, but the densities recorded were not determined until some months later, after remaining in tightly corked bottles, except in the case of allyl alcohol which was freshly distilled. The trimethylcarbinol was distilled over sodium, and the benzene was freed from thiophen by sulphuric acid. In the following table the boiling points are corrected to normal pressure and for emergent column error where necessary.

Liquid.	B. p.	D ₄ °.
Methyl alcohol	64·65° const.	0·81023
<i>n</i> -Propyl „	97·20—97·25°	0·82135
<i>iso</i> Propyl „	80·7 —81·4°	0·81873
Allyl „	97·06° const.	0·86911 *
<i>n</i> -Butyl „	117·5 „ „	0·82393
Dimethylethylcarbinol.....	102·30—102·33°	—
Benzene	80·08— 80·12°	—
Aniline	182·68—182·73°	—
	m. p. —5·95°	

* This density was previously given as D₀ in error (Wallace and Atkins, T., 1912, 101, 1963), as were other densities recorded in the same paper.

In the following tables are set forth the values of *C*, the molecular concentration of solute per 100 molecules of solvent, of Δ the depression of freezing point, and of *M* the molecular weight. In calculating these last, the value $K=58\cdot7$ (Ampola and Rimatori, *Gazzetta*, 1897, 27, i, 51) was employed.

Fig. 1 was constructed from these data.

Solute: water (M.W. 18).

<i>C</i> .	Δ .	<i>M</i> .
2·041	1·000°	22·5
4·303	1·957	24·7

Solute: *n*-propyl alcohol (M.W. 60), followed by water.

<i>C</i> .	Δ .	<i>M</i> .
0·499	0·327°	57·8
1·642	1·065	58·4
2·728	1·738	59·4
1·922 (water)	0·927	23·5

Solute: allyl alcohol (M.W. 58), followed by water.

<i>C</i> .	Δ .	<i>M</i> .
0·912	0·523°	63·9
3·584	1·970	66·6
3·487 (water)	1·400	28·3
1·036 (alcohol)	0·631°	60·1
2·305	1·332	63·4
2·882 (water)	1·301	25·2
4·768	2·072	26·1

Solute: trimethylcarbinol (M.W. 74), followed by water.

<i>C.</i>	Δ .	<i>M.</i>
0.346	0.300°	54.0
1.383	0.963	67.0
1.987	1.303	71.2
1.752 (water)	0.820	24.3
3.926	1.843	24.2

Solute: dimethylethylcarbinol (M.W. 88), followed by water.

<i>C.</i>	Δ .	<i>M.</i>
0.427	0.347°	63.4
1.059	0.706	66.1
2.180	1.380	87.7
2.770 (water)	1.260	25.0

The aniline, m. p. -5.95° , was found to give a eutectic point with water at -10.25° .

The association of allyl alcohol (M.W. 58) in benzene is shown by the following figures:

<i>C.</i>	Δ .	<i>M.</i>
0.915	0.979°	64.7
1.14	1.065	73.7
1.61	1.314	84.6
2.66	1.675	109.5

It is clear that the molecules are nearly all double ones at the higher concentrations. This behaviour is in marked contrast to that in aniline solution.

The addition of water was found to raise the freezing point by extracting alcohol. Making the assumption that water is quite insoluble in the dilute solution of allyl alcohol in benzene, it is possible to calculate the partition-coefficient of the alcohol between the two solvents. Water was added in successive small quantities, and the freezing point of the benzene in the heterogeneous mixture was determined after thorough stirring. From the curve obtained by plotting *C* against *M* in the above table, the amount of alcohol present in the benzene at each stage was determined, and the amount in the water was obtained by difference. In the following table are recorded the concentrations of alcohol in 100 grams of benzene and water respectively:

<i>C_B</i>	<i>C_W</i>	<i>C_W/C_B</i>
3.43	25.8	7.5
2.65	19.4	7.3
1.47	15.8	10.7
0.74	10.6	14.3

The above values are not of any great accuracy, as they are open to the errors of cryoscopic experiments with small quantities

of solute. The great alteration in the values of C_w/C_B are to be accounted for by the association of the alcohol in benzene, and to a less extent in aqueous solution. It is to be expected that with dilute solutions a constant value would be obtained. This, however, was foreign to our investigation, and was studied no further.

Below are recorded the data from which Fig. 2 was constructed, namely, the densities of the alcohols and their approximately equimolecular mixtures with water at various temperatures. The exact proportions of the mixtures have already been recorded in table I.

Methyl Alcohol.

Alone.		With water.	
t° .	D_4° .	t° .	D_4° .
0.0°	0.81023	0.0°	0.90030
12.05	0.79914	13.2	0.88505
45.3	0.76876	24.2	0.88241
		43.4	0.86726

n-Propyl alcohol.

0.0°	0.82135	0.0°	0.87001
13.4	0.81086	13.5	0.85974
47.3	0.78484	24.2	0.85102
		43.7	0.83468

*iso*Propyl alcohol.

0.0°	0.81873	0.0°	0.87069
11.8	0.80847	13.4	0.85970
45.3	0.78009	24.2	0.85117
		43.7	0.83337

Allyl alcohol.

0.0°	0.87028	0.0°	0.91224
		13.0	0.90125
		22.25	0.89340
		45.7	0.86984

n-Butyl alcohol.

0.0°	0.82393	0.0°	0.86144
13.4	0.81471	12.55	0.85216
47.3	0.79049	24.2	0.84339
		43.4	0.82836

The densities were determined by means of Perkin's modification of the Sprengel tube (T., 1884, 45, 444). It was found that even at the higher temperatures there was no appreciable loss by volatilisation during the time occupied by a measurement. At

room temperatures the loss of water from one tube was found to be only 0.0003 gram after sixteen hours, whilst a tube of greater capacity lost 0.0004 gram during the same period. The tubes were made of Jena 16^{III} glass, and the value 0.00000802 was taken as the linear coefficient of expansion in calculating their volumes at various temperatures. All weighings were reduced to weight in a vacuum.

This investigation was carried out in Prof. S. Young's private laboratory, Trinity College, Dublin, and we desire to thank him for the use of apparatus and for his interest in the work.

TRINITY COLLEGE,
DUBLIN.

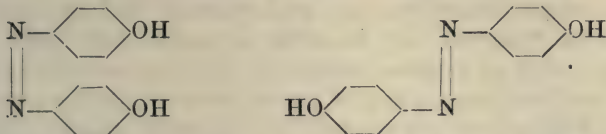
ST. JOHN'S COLLEGE,
AGRA N. INDIA.

CLVII.—*Isomerism of p-Azophenol.*

By PHILIP WILFRED ROBERTSON.

WITH regard to the chromoisomerism of the nitroanilines and certain other compounds investigated by Hantzsch, the objection can invariably be raised that as the differences disappear in solution the isomerism is merely a physical one. The problem is, however, different in the case of *p*-azophenol, our knowledge of which is due chiefly to Willstätter (*Ber.*, 1906, **39**, 3492; 1907, **40**, 1578). When prepared by the alkaline fusion of *p*-nitrophenol or by coupling the diazonium salt of *p*-aminophenol with phenol, the substance in the anhydrous state is green (α); when formed by the reduction of *p*-benzoquinoneazine, itself the oxidation product of *p*-azophenol, it exists as a red, anhydrous modification (β). An essentially important point is that simple physical treatment cannot affect a transformation of one into the other; from the most diverse solvents they invariably crystallise unchanged, as also after conversion into their alkali salts or hydrochlorides, or even after potassium hydroxide fusion. The two forms have appreciably different solubilities, but melt and decompose at the same temperature, namely 216°. Optically they are identical, yielding the same absorption spectrum (Hantzsch, *Ber.*, 1910, **43**, 2512). As a consequence this is regarded by Hantzsch as a case of homochromoisomerism, and the explanation of the difference is possibly to be sought in some stereochemical arrangement, for it has been frequently observed that *cis*- and *trans*-isomerides have the same absorption spectra (compare Hantzsch, *Ber.*, 1910, **43**, 1662). The two modifications would then

be formulated as below, a quinonoid structure in either case being impossible owing to the identity of the absorption spectra :

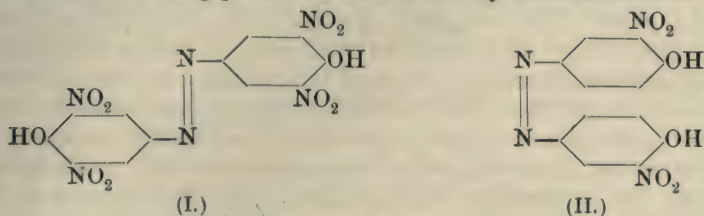


Willstätter has shown that both α - and β -*p*-azophenol yield one methyl and one benzoyl derivative, whereas on acetylation an α - and a β -compound are obtained. The acetyl derivative of β -*p*-azophenol is, however, unstable, and changes on keeping into the α -modification.

A further examination of the chemical reactions of the two *p*-azophenols has now been undertaken, with the hope of throwing more light on this unique kind of isomerism.

Nitration of α - and β -Azophenol.

According to Bohn and Heumann (*Ber.*, 1882, **15**, 3037), α -*p*-azophenol forms 2:4-dinitrophenol on nitration, even in acetic acid solution. It was found, however, if dilute solutions were employed and the temperature was prevented from rising, that an appreciable quantity of tetranitro-*p*-azophenol (I) was also produced. On the other hand, when β -*p*-azophenol was nitrated under the same conditions, even in the presence of a considerable excess of nitric acid, there was formed, not the tetranitro-derivative, but dinitro-*p*-azophenol (II), as well as the dinitrophenol; further, under comparable conditions the yield of substituted azophenol in the second case was much greater and that of dinitrophenol consequently correspondingly less, which indicates the stronger nature of the azo-linking in the β -compound. The results appear compatible with the assumption that α -*p*-azophenol has the *trans*-configuration, and that the β -compound is the *cis*-isomeride, the formation of the tetranitro-derivative being prevented in this case by steric hindrance :

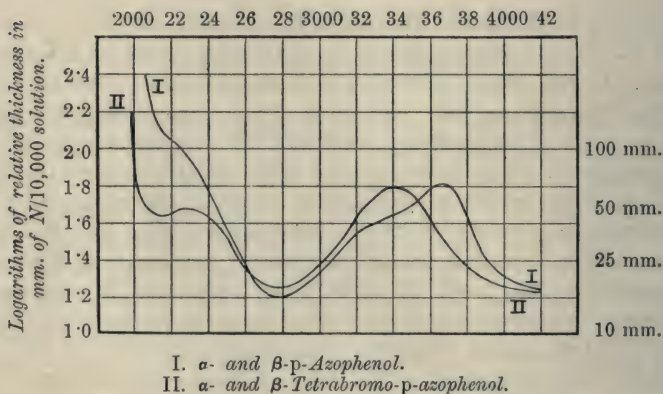


Dinitro-*p*-azophenol (II) readily absorbs bromine, with the formation of dibromodinitro-*p*-azophenol.

Bromination of α - and β -p-Azophenol.

A tetrabromo-derivative of α -p-azophenol has already been obtained by Weselsky and Benedikt (*Annalen*, 1879, **196**, 342); they describe it as a yellow substance, but give no melting point. By the cautious bromination of α -p-azophenol in dilute acetic acid solution a tetrabromo-derivative was obtained melting at 252° , whereas from β -p-azophenol a product melting at 271° was formed. Both these substances give identical absorption spectra * (see Fig. 1, where is also given the curve for α - and β -p-azophenol, Hantzsch, *Ber.*, 1910, **43**, 2514); the homochromoisomerism observed by Hantzsch in the case of *p*-azophenol persists, therefore, in its tetrabromo-derivatives, which would seem also to possess the *cis*- and *trans*-configurations.

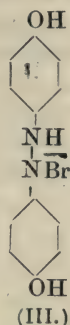
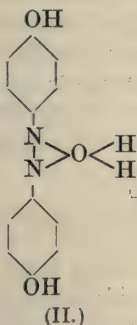
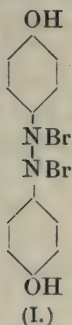
In the preparation of the bromo-derivatives the formation of

Oscillation frequencies.

varying amounts of a red insoluble compound was frequently noticed, and when the bromine was added rapidly this became the chief product. This substance, of a dark red colour, proved practically insoluble in all organic solvents, even in boiling acetic acid; advantage was accordingly taken of this property in order to obtain it in a pure condition. Stable in air, it lost hydrogen bromide slowly at 100° , changing to a green colour, and had all the properties of a perbromide, liberating iodine from potassium iodide solution, and having the composition $(C_6H_5ON)_2Br_2$. It thus appears to be *p*-azophenol perbromide (I), and its remarkable stability corresponds with that of the hydrate (II), which can be crystallised from benzene

* For these [photographs I am indebted to Dr. I. M. Heilbron, to whom my thanks are due.

unchanged, and that of the hydrobromide (III), discovered by Willstätter:

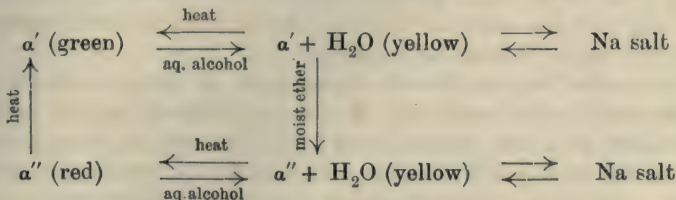


The mother liquors obtained in the preparation of the perbromide contained always a certain quantity of tetrabromo-*p*-azophenol, and it was the isomeride melting at 271°, whether one proceeded from α - or from β -azophenol. Under these conditions, therefore, a transformation must have occurred.

The Physical Isomerism of α -p-Azophenol.

The green anhydrous α -*p*-azophenol forms a stable yellow hydrate containing one molecule of water; if this is boiled with moist ether (Willstätter, *loc. cit.*) there is obtained on evaporation a yellow hydrate differing from the former in that it yields a red anhydrous modification. It has now been found that this red substance has a definite transition temperature into the green at about 50°. The two forms also tend to persist in solution; the hydrate which gives the red modification on heating can be crystallised from solvents such as methyl or ethyl alcohol, and even converted into its sodium salt, and recovered unchanged. The same is also true for the other hydrate, although in this case traces of the second form frequently appear.

The transformation of the different modifications of α -*p*-azophenol may then be summarised as follows:



On no occasion in a very large number of experiments was there any indication of a change into β -*p*-azophenol; the alleged trans-

formation (Willstätter and Beuf, *loc. cit.*) of α -*p*-azophenol by leaving its alkaline solution in contact with its own weight of the β -compound, smaller quantities of which did not bring about the change, consequently appears doubtful.

From the evidence on the whole this isomerism of α -*p*-azophenol seems merely physical, and the persistence of the two forms in solution is possibly due to the influence of a catalyst, which stabilises the one or the other.

EXPERIMENTAL.

Tetranitro-p-azophenol.—Three grams of α -*p*-azophenol were dissolved in 150 c.c. of acetic acid, and a slight excess of the calculated quantity of nitric acid in the same solvent was slowly added. Yellow crystals began almost immediately to separate, and were collected after leaving overnight; the yield of the crude product was in two experiments about 10 per cent. of the theoretical. After recrystallisation from hot acetic acid the compound melted sharply at 230° :

0.0734 gave 13.2 c.c. N_2 at 17° and 754 mm. $N=21.1$.

$C_{12}H_6O_{10}N_6$ requires $N=21.3$ per cent.

In the mother liquor there was found a considerable quantity of dinitrophenol melting at 113° . According to the experiments of Bohn and Heumann (*loc. cit.*), this substance was the only product of the reaction.

Dinitro-p-azophenol.— β -*p*-Azophenol was nitrated in the manner described above; the product was in this case the dinitro-derivative, and dinitrophenol was discovered in the mother liquor. It seemed possible that there might not have been sufficient nitric acid present for the complete nitration; consequently, the experiment was repeated with a considerably larger excess of nitric acid, and this was added more quickly. The same product was obtained, melting as before after recrystallisation from acetic acid constantly at 240° :

0.1859 gave 29.4 c.c. N_2 at 15° and 755 mm. $N=18.6$.

$C_{12}H_8O_6N_4$ requires $N=18.4$ per cent.

The yield of the crude product was in each experiment somewhat more than 20 per cent. of the theoretical, a considerably greater yield than in the case of α -*p*-azophenol.

Dibromodinitro-p-azophenol.—One gram of dinitro-*p*-azophenol was dissolved in hot acetic acid containing sufficient sodium acetate to combine with the hydrobromic acid liberated on bromination and treated with a dilute acetic acid solution of bromine in slight excess. The colour of the bromine immediately disappeared, and at the same time the new compound began to separate. The substance, which was obtained in a quantitative yield, melted at 282° :

0.1353 gave 14.6 c.c. N_2 at 20° and 752 mm. $N=12.4$.

$C_{12}H_6O_6N_4Br_2$ requires $N=12.1$ per cent.

α -Tetrabromo-p-azophenol.—Ten grams of α -p-azophenol and 8 grams of anhydrous sodium acetate were dissolved in acetic acid, and to the cold solution was added cautiously with constant stirring a dilute solution of 5 c.c. of bromine in acetic acid. The substance which separated was collected, and the residue extracted with boiling acetic acid; on cooling a crop of crystals was obtained melting at 240° , and in two subsequent recrystallisations the melting point was 252° , the melting occurring with decomposition:

0.0890 gave 0.1260 AgBr. $Br=60.2$.

$C_{12}H_6O_2N_2Br_4$ requires $Br=60.4$ per cent.

When, however, the bromine solution is more concentrated and added all at once, a red, insoluble compound is precipitated, and in the filtrate β -tetrabromo-p-azophenol, melting at 271° , is found, so that under these conditions there is a transformation of the α -compound.

β -Tetrabromo-p-azophenol.—This substance is prepared from β -p-azophenol by performing the bromination in the manner described above. In one experiment the product of the first crystallisation melted at 264° , and after further recrystallisation at 271° and 272° , in each case with decomposition:

0.1022 gave 0.1434 AgBr. $Br=59.8$.

$C_{12}H_6O_2N_2Br_4$ requires $Br=60.4$ per cent.

Like the α -derivative, it was sparingly soluble in cold acetic acid, from which solvent it could be conveniently crystallised.

p-Azophenol Perbromide.—When a concentrated acetic acid solution of bromine is added quickly to a saturated solution of α - or β -azophenol in the same solvent, a dense red precipitate is obtained. This was found to be insoluble in organic solvents, even in boiling acetic acid. It was consequently obtained free from impurity by being extracted several times in this manner. The substance was soluble in aqueous alkalis, from which solutions it could be reprecipitated by acids, and had the power of liberating iodine from potassium iodide:

0.2253 gave 15.2 c.c. N_2 at 23° and 756 mm. $N=7.8$.

$C_{12}H_{10}O_2N_2Br_2$ requires $N=7.6$ per cent.

When heated at 100° p-azophenol perbromide slowly changed to green with the loss of hydrogen bromide; all of the bromine, however, was not evolved, even after prolonged heating, and it appeared that a mixture of substances had been produced.

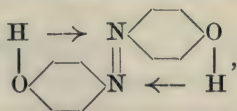
The Isomerism of α -p-Azophenol.—As ordinarily prepared p-azophenol is obtained as a yellow hydrate, which loses water to

form a green modification. If the yellow hydrate is boiled with moist ether or moist acetic acid, and sometimes on mere keeping, it forms a new hydrate yielding a brick-red anhydrous variety, which on heating changes back into the green. The approximate transition point was determined from the following observations. In a desiccator the red variety could be preserved indefinitely: heated in dry light petroleum boiling at 40° it was not altered after forty-eight hours; when it was heated in dry light petroleum boiling at 60° it was found that after an hour or two particles of the green had already begun to appear. The transition temperature is therefore in the neighbourhood of 50° , and this seems merely a case of physical isomerism.

It is nevertheless surprising that these two varieties can pass into solution, for example, in methyl and ethyl alcohol, and be recovered again unchanged. This was also true even if they had been converted into their sodium salts, although in this case the green modification tended to change to some extent into the red. The method of testing was always the same, namely, to heat the yellow hydrate on a watch-glass in a steam-oven. At this temperature the change from the red to the green is still comparatively slow, and it was invariably found that the red or green colour flashed up distinctly in five to ten minutes.

The apparent persistence of the two forms in solution seems almost to indicate a chemical isomerism; yet as to the nature of this there is no evidence. It might be conceivable, however, that a trace of some catalyst is necessary to stabilise the one or the other form, and that this is not decomposed by solution. Some red *α-p*-azophenol, dissolved in boiling acetic acid which was immediately chilled in ice, showed no signs of transformation into the green after recovery from the solvent. It was also found impossible to effect the conversion of the red in solution by chemical means, for example, with a trace of sulphur dioxide. On the whole, the facts seem to point to the presence of a trace of easily oxidisable impurity, which stabilises the hydrate giving the green modification.

From a consideration of the formula of *p*-azophenol,



it will be noticed that there is a tendency for both hydroxylic hydrogen atoms to migrate to nitrogen, forming thus a quinonoid substance. It is perhaps not inconceivable that there might be two positions of greater stability occupied by these wandering hydrogen atoms, corresponding with the two *α*-modifications. That there is

only one β -modification could be explained by the fact that in the *cis*-isomeride the hydrogen migration would be hindered sterically.

This investigation is being extended to the methyl derivatives of *p*-azophenol.

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CLVIII.—*The Azo-derivatives of 2:2'-Diphenol.*

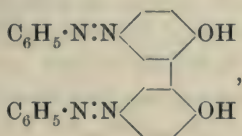
By PHILIP WILFRED ROBERTSON and OSCAR LISLE BRADY.

It was first pointed out by Hewitt (*Ber.*, 1895, **28**, 799) that hydroxyazo-compounds tended to form characteristic hydrates which were of different colour from the original compounds. A list of such cases is given by Hantzsch and Robertson (*Ber.*, 1910, **43**, 106), and it is noteworthy that there is a general tendency for the hydrates to crystallise with half a molecule of water.

That this characteristic behaviour depends on some inherent property of the azo-grouping is supported by the fact that the alkali salts of these compounds also frequently crystallise with half a molecule of solvent of crystallisation. In some cases the hydrates are of quite exceptional stability, as, for example, in the case of benzeneazoresorcinol, which was for a long time regarded as existing in two modifications. Quite recently, however, Hantzsch (*Ber.*, 1913, **46**, 1556) has shown that the difference depends on the fact that one modification contains water, which is removed only after long heating at 120°.

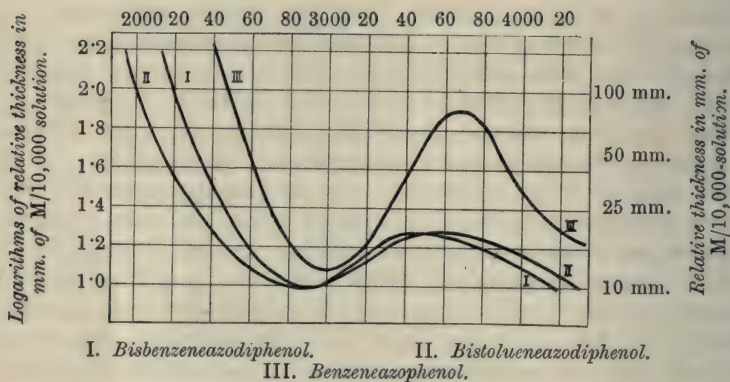
Now that the nature of this substance has been settled, there appears to remain only one genuine case of a simple hydroxyazo-compound existing in two modifications, neither of which is a hydrate, and this substance is naphthaleneazophenol. McPherson and Gore (*Amer. Chem. J.*, 1901, **25**, 491) have shown that the ordinary yellow variety, on heating to 130°, changes its colour to red without loss of weight, and that this red modification may be recrystallised from petroleum unchanged.

In the course of some investigations on the azo-derivatives of 2:2'-diphenol, it was observed that 5:5'-bisbenzeneazo-2:2'-diphenol:



existed in a red and yellow modification, each containing half a molecule of water of crystallisation. The exact conditions which determined the stability of the two hydrates could not be ascertained, and both varieties were frequently observed to separate together, for example, on acidifying the aqueous alkaline solution, or on recrystallising from such different solvents as alcohol and glacial acetic acid. These hydrates were further characterised by their exceptional stability; they could be heated to 100° without losing water, and could be recrystallised from chloroform unchanged. On loss of water, which occurred slowly at 160° , the colour in each case was unchanged. The two varieties had the same melting point, namely, 184° , the yellow changing, just before melting, into the red. This, then, seems an ordinary case of

Oscillation frequencies.



polymorphism, although the determining factor may be due possibly to stereoisomerism or the tendency of one or other variety to assume the quinonoid constitution. That this substance has the azo-constitution is made evident by the examination of its spectrum.

The deep band characteristic of the azo-group, shown by the curve for benzeneazophenol, which is also included, and entirely different from that observed in the corresponding quinonoid compounds, is noticed to be considerably flattened in the two bisazo-compounds that were photographed.* The reason for this is probably to be sought in the fact that the residual affinities of the azo-groupings in different parts of the same molecule tend to neutralise each other, so that the characteristic band which they cause in the spectrum is not so evident.

* We have much pleasure in expressing our indebtedness to Dr. I. M. Heilbron for these photographs.

This ready tendency to form two modifications was not noticed in the other bisazo-compounds of 2:2'-diphenol, although the dibromo-derivative of bisbenzeneazo-2:2'-diphenol was found to change under the influence of light from yellow to red when kept in a sealed tube under toluene. On the other hand, the tendency to form hydrates was frequently observed. Thus, 5:5'-bis-*p*-chlorobenzeneazo-2:2'-diphenol formed a red hydrate, which was stable at 100°, losing its molecule of water at 160° to form the yellow, anhydrous compound, and the isomeric *o*-chloro-compound formed a hydrate which was so stable that its water could be driven off only on melting. A further point of interest concerning these compounds was that substituents in the benzene nucleus tended to prevent the formation of bisazo-2:2'-diphenols, probably owing to steric hindrance. Thus, aniline and *o*-chloroaniline gave good yields of the bisazo-compounds, whereas *p*-toluidine and *p*-chloroaniline reacted less readily, producing also some monoazo-compound, and in the case of α -naphthylamine the monosubstituted derivative was the only product of the reaction.

This substance, 5- α -naphthaleneazo-2:2'-diphenol, was noticeable in that it formed a green hydrate, a colour rarely observed among azo-compounds.

Owing to the peculiar nature of the isomerism of *p*-azophenol, a substance of the constitution:



was prepared from *p*-aminophenol and 2:2'-diphenol. This compound was apparently obtained, although in a poor yield; unfortunately its slight solubility and its very high melting point (above 300°) caused difficulties which prevented a more detailed examination.

EXPERIMENTAL.

5:5'-Bisbenzeneazo-2:2'-diphenol.—A solution of 10 grams of aniline was diazotised and added slowly with constant stirring to a well-cooled solution of 10 grams of diphenol in 50 c.c. of 2*N*-sodium hydroxide diluted to about three litres. The mixture was left overnight, when the hydroxyazo-compound separated as a yellow precipitate. This was collected and freed from small quantities of tarry matter by solution in ammonia and reprecipitation with acid. The crude substance was crystallised from chloroform and light petroleum, and was obtained as a deep red, crystalline powder, which retained traces of chloroform even after

drying at 110° , but was obtained pure by recrystallisation from glacial acetic acid.

When crystallised from diluted alcohol, a pale yellow modification was obtained, which also separated at times from chloroform or acetic acid, often together with the red form. There seemed to be no method of controlling the form in which the compound separated, although chloroform seemed to favour the production of the red modification. From whatever solvent the substance separated, each modification always contained half a molecule of water.

The compounds were dried in a steam oven at 110° .

Red modification :

0.1275 gave 0.3352 CO_2 and 0.0546 H_2O . $\text{C}=71.6$; $\text{H}=4.7$.

0.2042, heated to 160° for four hours, lost 0.0043. $\text{H}_2\text{O}=2.1$.

Yellow modification :

0.1238 gave 0.3258 CO_2 and 0.0546 H_2O . $\text{C}=71.7$; $\text{H}=4.9$.

0.2004, heated to 160° for four hours, lost 0.0044. $\text{H}_2\text{O}=2.2$.

$\text{C}_{24}\text{H}_{18}\text{O}_2\text{N}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ requires $\text{C}=71.4$; $\text{H}=4.7$; $\text{H}_2\text{O}=2.2$ per cent.

Both forms melted at 184° , the yellow changing to the red just before melting.

Hydrochloride of 5 : 5'-Bisbenzeneazo-2 : 2'-diphenol.—The base was dissolved in dry chloroform, and the solution saturated with dry hydrogen chloride. The hydrochloride separated as a bright red, crystalline powder, which was collected, washed with light petroleum, and dried in the air :

0.1604 gave 0.0995 AgCl . $\text{Cl}=15.3$.

$\text{C}_{24}\text{H}_{18}\text{O}_2\text{N}_4 \cdot 2\text{HCl}$ requires $\text{Cl}=15.2$ per cent.

The hydrochloride has no definite melting point, and is almost insoluble in concentrated hydrochloric acid.

3 : 3'-Dibromo - 5 : 5' - bisbenzeneazo - 2 : 2' - diphenol.—The bisbenzeneazodiphenol was dissolved in glacial acetic acid, anhydrous sodium acetate added, and then cautiously the requisite quantity of bromine dissolved in acetic acid. The bromo-compound separated almost at once, and was crystallised from glacial acetic acid, separating in golden crystals, melting at 222° :

0.1042 gave 0.1988 CO_2 and 0.0302 H_2O . $\text{C}=52.1$; $\text{H}=3.2$.

$\text{C}_{24}\text{H}_{16}\text{O}_2\text{N}_4\text{Br}_2$ requires $\text{C}=52.1$; $\text{H}=3.2$ per cent.

A solution of this substance in benzene in a sealed tube exposed to light slowly deposited dark red crystals.

5 : 5'-Bis-p-tolueneazo-2 : 2'-diphenol.—This substance was prepared in an analogous way to the unsubstituted compound from p-toluidine and diphenol. The product was only partly soluble in

ammonia, and the insoluble residue, after treatment with hydrochloric acid, gave the most satisfactory crop of pure substance after crystallisation from glacial acetic acid. The portion soluble in ammonia appeared to contain the monoazo-compound, which, however, could not be obtained in a pure condition:

0.1879 gave 20.8 c.c. N_2 at 19° and 760 mm. $N=13.0$.

0.2114, heated to 160° for twelve hours, lost 0.0041. $H_2O=1.9$.

$C_{26}H_{22}O_2N_4, \frac{1}{2}H_2O$ requires $N=12.9$; $H_2O=2.0$ per cent.

This compound forms pale yellow crystals, melting at 228° .

5: 5'-*Bis-p-chlorobenzeneazo-2: 2'-diphenol*.—This compound was obtained from *p*-chloroaniline and diphenol in the usual way, and was isolated from the portion insoluble in ammonia. It was crystallised from glacial acetic acid, and then from alcohol, when it was obtained in red crystals, melting at 226° :

0.2064 gave 20.8 c.c. N_2 at 17° and 754 mm. $N=11.8$.

0.3354 lost at 160° 0.0118. $H_2O=3.5$.

$C_{24}H_{14}O_2N_4Cl_2, H_2O$ requires $N=11.6$; $H_2O=3.7$ per cent.

The anhydrous substance was yellow.

5-*p-Chlorobenzeneazo-2: 2'-diphenol*.—This compound was obtained from the ammonia extract in the previous preparation. This was acidified with hydrochloric acid, the precipitate dissolved in glacial acetic acid, and reprecipitated by the cautious addition of water:

0.1160 gave 0.2800 CO_2 and 0.0451 H_2O . $C=65.9$; $H=4.3$.

$C_{18}H_{13}O_2N_2Cl$ requires $C=66.5$; $H=4.0$ per cent.

The compound is a yellow, crystalline powder, melting at 163° . A further proof that only one of the hydrogen atoms in the diphenol had been replaced in this compound was furnished by the fact that on bromination it yielded a tribromo-derivative.

5-*p-Chloro-3: 3': 5'-tribromobenzeneazo-2: 2'-diphenol*.—This was obtained by the bromination of the above compound in glacial acetic acid in the presence of anhydrous sodium acetate, and recrystallising the product first from glacial acetic acid and then from alcohol. It is a reddish-brown, crystalline powder, melting at 197° :

0.1402 gave 0.1991 CO_2 and 0.0259 H_2O . $C=38.7$; $H=2.0$.

$C_{18}H_{10}O_2N_2ClBr_3$ requires $C=38.4$; $H=1.7$ per cent.

5: 5'-*Bis-o-chlorobenzeneazo-2: 2'-diphenol*.—This substance was obtained as before from diphenol and *o*-chloroaniline, the yield in this case being particularly good, and the product completely soluble in ammonia. The ammoniacal solution was acidified with hydrochloric acid, and the precipitate crystallised from acetic acid, when it was obtained in yellow crystals, melting at 218° :

0.1182 gave 0.2653 CO_2 and 0.0415 H_2O . $\text{C}=61.2$; $\text{H}=3.9$.

0.1177 „ 0.2636 CO_2 „ 0.0407 H_2O . $\text{C}=61.0$; $\text{H}=3.8$.

$\text{C}_{24}\text{H}_{14}\text{O}_2\text{N}_4\text{Cl}_{2.5}\text{H}_2\text{O}$ requires $\text{C}=61.0$; $\text{H}=3.6$ per cent.

It is of interest that these compounds retain water even at high temperatures; in the case of this substance the water appears to be driven off only on melting.

5: 5'-Bis-*p*-hydroxybenzeneazo-2: 2'-diphenol.—It was found that *p*-hydroxybenzenediazonium chloride would not condense with diphenol in an acid or neutral solution, so the diphenol was dissolved in sufficient alkali to leave the reaction mixture faintly alkaline. After twenty-four hours, excess of dilute sulphuric acid was added, and the red precipitate collected and crystallised from glacial acetic acid. The product was a dark red, crystalline powder, melting above 330° :

0.1346 gave 0.3334 CO_2 and 0.0514 H_2O . $\text{C}=67.5$; $\text{H}=4.2$.

$\text{C}_{24}\text{H}_{18}\text{O}_4\text{N}_4$ requires $\text{C}=67.5$; $\text{H}=4.2$ per cent.

The further investigation of this substance was prevented by the very small yield obtained and its extreme insolubility.

5-Naphthaleneazo-2: 2'-diphenol.—This compound, prepared from diphenol and α -naphthylamine, was purified by solution in toluene and precipitation with light petroleum; it formed yellow crystals, melting at 150° :

0.1418 gave 10.8 c.c. N_2 at 23° and 758 mm. $\text{N}=8.7$.

$\text{C}_{22}\text{H}_{16}\text{O}_2\text{N}_2$ requires $\text{N}=8.2$ per cent.

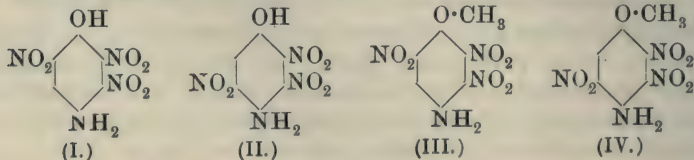
When obtained from its ammonium salt by the action of dilute acids, there was formed a green hydrate, which was unstable in air. A rapidly performed analysis indicated the presence of one molecule of water.

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CLIX.—The Constitution of the Trinitro-*p*-aminophenols and Trinitro-*p*-anisidines.

By RAPHAEL MELDOLA and FRÉDÉRIC REVERDIN.

OF the two possible trinitro-derivatives of *p*-aminophenol (I and II),



one was first obtained as an acetyl derivative in 1906 (T., **89**, 1935), and the free base was described by one of the authors and J. G. Hay three years later (T., 1909, **95**, 1380). The first of the corresponding trinitroanisidines was prepared by one of the authors in 1909 (*Arch. Sci. phys. nat.*, [iv], **27**, 383), and the second by methylating the trinitro-*p*-acetylaminophenol above referred to and hydrolysing the acetyl derivative (Meldola and Kuntzen, T., 1910, **97**, 444). The isomerism of the two trinitroanisidines is indicated by their melting points and general properties:

Reverdin's:	m.p. acetyl derivative, 242°; free base, 127—128°
Meldola & Kuntzen's:	„ „ „ 194°; „ 138—139°

The chief interest attaching to these trinitro-compounds is the extreme mobility of one of the nitro-groups, a property which has been utilised by one of the authors and his colleagues in a series of synthetical operations resulting in the formation of iminazoles and their derivatives. From this class of syntheses it follows that the mobile nitro-group is ortho with respect to the acetylaminogroup in the trinitroacetylaminophenol and its corresponding trinitroacetoanisidine (m. p. 194°), and it has accordingly been assumed throughout that it is the nitro-group in position 3 which is mobile. Further research, the results of which will be made known at a later period, has amply confirmed this assumption. With respect to the trinitroanisidine of m. p. 127° it has been shown by the authors in a previous communication (T., 1910, **97**, 1204) that on diazotisation the 3-nitro-group is also eliminated. On the other hand, it appears from the results made known in the present paper that under the influence of basic decomposing agents it is the 2-nitro-group which is replaced (see also *Arch. Sci. phys. nat.*, 1910, [iv], **29**, 476). We have thus arrived at the general conclusion that in trinitroacetylaminophenol and the corresponding trinitroanisidine (m. p. 138—139°) and trinitroacetoanisidine (m. p. 194°) it is always the 3-nitro-group which is mobile, as has hitherto been established, whereas in the isomeric trinitroanisidine (m. p. 127°) the 2-nitro-group is mobile under the influence of basic reagents and the 3-nitro-group under the influence of the neighbouring diazonium group.*

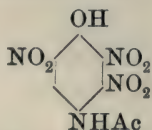
The constitution assigned to these two sets of trinitro-derivatives has hitherto been based upon the indirect evidence which led to the original trinitroacetylaminophenol being regarded as the 2 : 3 : 5-trinitro-compound (No. II above). Although frequently summarised

* A similar conclusion has been arrived at with respect to the corresponding 2 : 3 : 5-trinitro-*p*-phenetidine by Ludwik Fürstenberg, *Sur les Dérivés Nitrés de la p-Phénétidine*, a Thesis recently (1913) presented to the Faculty of Science of the University of Geneva.

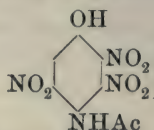
in former papers, we think it desirable to set forth this evidence once again, because the present investigation makes it evident that the original compound is the 2:3:6-trinitro-derivative, and the position of the third nitro-group in the corresponding trinitro-anisidine must accordingly be modified, whereby the isomeric trinitroanisidine of m. p. 127° becomes the 2:3:5-trinitro-derivative, as was surmised by one of the authors at the time of its discovery (*Arch. Sci. phys. nat.*, 1909, [iv], **27**, 396), although no direct evidence of this constitution was adducible at the time. The evidence which led to the placing of the third nitro-group in position 5 in the first discovered trinitroacetylaminophenol is briefly as follows:

Diacetyl-*p*-aminophenol, 3-nitrodiacetyl- and monoacetyl-*p*-aminophenol, and 2:3-dinitro-*p*-acetylaminophenol (T., 1907, **91**, 1481) all give the trinitro-compound on extreme nitration under all conditions. On the other hand, 2:6-dinitro-*p*-acetylaminophenol (acetyl*isop*ieramic acid) fails to give the trinitro-compound under any conditions. This observation has been verified by numerous later experiments made in connexion with the present research. The nitration of diacetyl-*p*-aminophenol by fuming nitric acid gives first the 3-nitro-derivative and then the 3:5-dinitro-compound (Reverdin and Dresel, *Arch. Sci. phys. nat.*, 1905, [iv], **19**, 353). By more energetic nitration with a mixture of nitric and sulphuric acids, however, the same trinitro-compound is formed, so that under certain conditions it appears that the 5-nitro-group is capable of migrating to position 6, or else that the preliminary removal of the *O*-acetyl leads to the subsequent nitration of the 3-nitro-4-acetylaminophenol, and this last compound is known to give the original trinitro-compound on further nitration. The accumulated indirect evidence thus indicated position 5 for the third nitro-group in trinitroacetylaminophenol and the corresponding trinitroanisidine.

The direct proof of the position 6 for the third nitro-group which is submitted in the present paper has led to further search for the missing 2:3:5-trinitro-compound, and this, as will be seen from the experimental part, has now been obtained as an acetyl derivative by the regulated nitration of 3:5-dinitro-mono- or -di-acetyl-*p*-aminophenol. The revised formulæ are accordingly:



M. p. 178° ; free base, m. p. 145° ,
with decomposition.
Corresponding methoxy-compound,
m. p. 194° .



M. p. 193° , with decomposition.
Free base unknown.
Corresponding methoxy-compound,
m. p. 242° .

The extreme mobility of the 3-nitro-group in the 2:3:6-trinitro-compound is no doubt connected with the fact that this group is ortho- with respect to one nitro-group, and para- with respect to the other, thus conforming with the general rule which regulates the elimination of a nitro-group on diazotisation of the dinitro-anisidines (T., 1906, **89**, 923; 1907, **91**, 1474; see also Crossley and Pratt with reference to the trinitro-*o*-xylenes, this vol., p. 982).

That one of the nitro-groups in the 2:3:5-series is also mobile appears from the reactivity of the trinitroanisidine with bases (*Arch. Sci. phys. nat.*, 1910, [iv], **29**, 476), but the conditions which determine this mobility will require further investigation.

EXPERIMENTAL.

Constitution of the Trinitro-p-anisidine of m. p. 127°.

An attempt was first made to obtain the trinitroaminophenol from the above compound by demethylation by heating the substance with 30 per cent. hydrochloric acid in a sealed tube for three hours at 150°. A mixture of products was obtained, partly phenolic and partly non-phenolic, and containing chlorine. The results were not sufficiently definite to throw light on the main question of the position of the nitro-groups, but they indicate that partial demethylation takes place under these conditions, and that the products formed are due to secondary reactions of the unstable trinitroaminophenol.

An attempt to eliminate the amino-group by the diazo-method was also unsuccessful from the point of view of determining the constitution of the trinitroanisidine. In this case, however, certain definite products were obtained which prove at any rate that a nitro-group is also eliminated on diazotisation, and thus confirming the result made known in our former paper (T., 1910, **97**, 1204). The constitution of these products has yet to be determined, but their general characters are sufficiently definite to warrant their preliminary description pending the further development of this part of the research.

Trinitroanisidine was dissolved in concentrated sulphuric acid and diazotised at -5° with solid sodium nitrite in the usual way. The diazonium salt was decomposed by prolonged boiling with alcohol, the excess of alcohol distilled off, the residual solution diluted with water, and made alkaline with sodium carbonate, and then extracted with ether. The ethereal extract, on evaporation, left a small quantity of an oily, uncrystallisable residue, which may have been the methyl ether of the trinitrophenol. The alkaline solution, on acidifying with hydrochloric acid and extraction with ether, gave, on evaporation of the solvent, a con-

siderable quantity (70 per cent. of the weight of trinitroanisidine) of a crystalline product, consisting apparently of a mixture of two isomeric compounds. These compounds were separated by crystallisation from hot water, the solution on cooling depositing a crop of ochreous crystals, which by further crystallisation from benzene were obtained as slender, pale yellow needles, melting at 181° . The aqueous mother liquor contained a more soluble substance, which separated on the addition of hydrochloric acid in fine, lemon-yellow needles, melting at 114° :

0.1308 (m. p. 181°) gave 0.1884 CO_2 and 0.0349 H_2O . $\text{C}=39.28$;
 $\text{H}=2.96$.

0.1208 (m. p. 181°) gave 13.3 c.c. N_2 (moist) at 18° and 766 mm.
 $\text{N}=12.76$.

0.1174 (m. p. 114°) gave 0.1690 CO_2 and 0.0312 H_2O . $\text{C}=39.25$;
 $\text{H}=2.95$.

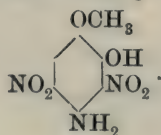
0.0816 (m. p. 114°) gave 10.2 c.c. N_2 (moist) at 27° and 720 mm.
 $\text{N}=13.04$.

These numbers agree with the formula of a dinitrohydroxy-methoxybenzene, $\text{HO}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{O}\cdot\text{CH}_3$, which requires $\text{C}=39.25$;
 $\text{H}=2.80$; $\text{N}=13.08$ per cent.

Both products give, on reduction, diamines which have certain of the characters of ortho-diamines, but further evidence on this point will be required.

4: 6-Dinitroguaiacol from the Trinitroanisidine.

It has been shown in former communications that in compounds containing a mobile nitro-group the latter can in some cases be replaced by hydroxyl by boiling the substance with aqueous sodium acetate. This was shown to be the case with 2:3:6-trinitro-quinonediazide (formerly formulated as the 2:3:5-trinitro-compound; T., 1909, **95**, 1384) and with the trinitroanisidine of m. p. 127° now under consideration (*Arch. Sci. phys. nat.*, 1910, [iv], **29**, 481). The compound resulting from the action of aqueous sodium acetate on the trinitroanisidine is a phenolic substance crystallising from methyl alcohol in brown scales or in needles with green, metallic lustre, and melting at 163 – 164° . The properties of the compound and the analyses of the salts and derivatives indicate that it is 4:6-dinitro-5-aminoguaiacol, the constitution, as indicated below, being determined by its yielding 4:6-dinitroguaiacol on elimination of the amino-group:



It thus appears that the 2-nitro-group is the mobile group under the conditions specified. The barium salt crystallises in brown needles:

0.1035 gave 0.0380 BaSO_4 . $\text{Ba} = 21.38$.

$(\text{C}_7\text{H}_6\text{O}_6\text{N}_3)_2\text{Ba}, 2\text{H}_2\text{O}$ requires $\text{Ba} = 21.78$ per cent.

The *diacetyl* derivative crystallises in pale yellow needles, melting at 134° :

0.1278 gave 15.5 c.c. N_2 (moist) at 16° and 713 mm. $\text{N} = 13.19$.

$\text{C}_{11}\text{H}_{11}\text{O}_8\text{N}_3$ requires $\text{N} = 13.41$ per cent.

The amino-group was replaced by hydrogen by decomposing the diazonium sulphate with alcohol in the usual way, and there was obtained as the main product a dinitroguaiacol, which, when pure, crystallised from water in pale yellow needles, melting at 122° . Purification was effected through the barium salt, which crystallises from water in brownish-yellow needles:

0.1777 gave 0.0643 BaSO_4 . $\text{Ba} = 21.40$.

$(\text{C}_7\text{H}_5\text{O}_6\text{N}_2)_2\text{Ba}, 4\text{H}_2\text{O}$ requires $\text{Ba} = 21.62$ per cent.

The barium salt, on decomposition by hydrochloric acid, gave the free dinitroguaiacol above described:

0.1544 gave 0.2227 CO_2 and 0.040 H_2O . $\text{C} = 39.01$; $\text{H} = 2.87$.

0.0895 „ 10.3 c.c. N_2 (moist) at 14° and 716 mm. $\text{N} = 12.70$.

$\text{C}_7\text{H}_6\text{O}_6\text{N}_2$ requires $\text{C} = 39.25$; $\text{H} = 2.80$; $\text{N} = 13.08$ per cent.

The constitution of this dinitroguaiacol was determined by comparing it with a specimen of the same compound prepared by the direct nitration of acetylguaiacol, a mixture of the two having the same melting point (122°), and also by conversion by demethylation into the corresponding dinitrocatechol. The latter was obtained by heating the dinitroguaiacol with 30 per cent. hydrochloric acid in a sealed tube for three hours to $145\text{--}150^\circ$; it crystallised in yellow needles melting at 164° , and proved to be identical with the 3:5-dinitrocatechol prepared by the nitration of diacetylcatechol (Nietzki and Moll, *Ber.*, 1893, **26**, 2183). The dinitroguaiacol was also converted by the methylation of its silver salt by methyl iodide into the corresponding dinitroveratrole, which melted at 101° , and proved to be identical with the compound obtained by Blanksma by the action of sodium methoxide on 2:3:5-trinitroanisole (*Rec. trav. chim.*, 1904, **23**, 112).^{*} The constitution of the trinitroanisidine of m. p. 127° as the 2:3:5-trinitro-compound is thus definitely proved, and the mobility of the 2-nitro-group at the same time established.

^{*} M. Blanksma has been good enough to enable this comparison to be made by sending a specimen of his compound.

Syntheses with 2:3:5-Trinitroanisidine.

The mobility of the 2-nitro-group in the above trinitroanisidine is shown also by the readiness with which condensation products are obtained by the action of bases, etc. Some of these compounds are described below:

3:5-Dinitro-2:4-diaminoanisole is readily formed by heating an alcoholic solution of the trinitroanisidine with alcoholic ammonia on the water-bath. The compound separates as a red powder, which, after crystallisation from alcohol or acetic acid, consists of minute, reddish-violet crystals, melting about 250°, and but sparingly soluble in the solvents named:

0.1707 gave 35.8 c.c. N₂ (moist) at 18° and 762 mm. N=24.18.

C₇H₈O₅N₄ requires N=24.56 per cent.

The *diacetyl* derivative of the above compound is formed by the action of acetic anhydride in presence of a trace of sulphuric acid. It crystallises from nitrobenzene or from alcohol, in which solvents it is but sparingly soluble, in small, white needles, melting above 260°:

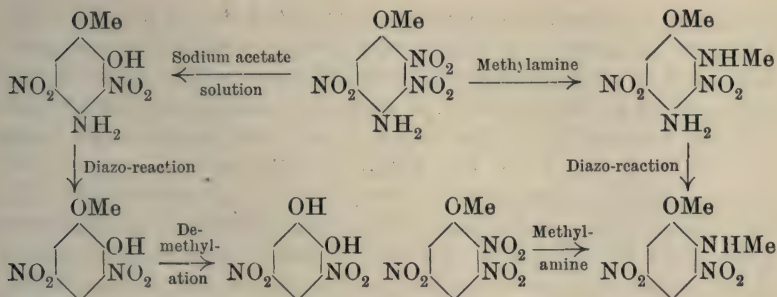
0.1631 gave 24.9 c.c. N₂ (moist) at 17° and 759 mm. N=17.61.

C₁₁H₁₂O₇N₄ requires N=17.94 per cent.

The diamine diazotises but imperfectly, and the bisdiazonium salt, on boiling with alcohol, yielded a small quantity of a dinitroanisole, crystallising in fine, orange needles, melting at 104°, and which was proved to be identical with 3:5-dinitroanisole.

The corresponding 2-methylamino-derivative (m. p. 199—200°), prepared by the action of methylamine on the trinitroanisidine, has already been described by one of the authors (*Arch. Sci. phys. nat.*, 1910, [iv], **29**, 481). On replacing the amino-group in this compound by hydrogen by the diazo-method, there is obtained a dinitromethylaminoanisole, crystallising in fine, red needles, melting at 167—168°. This substance was identified as 3:5-dinitro-2-methylaminoanisole (Grimaux and Lefèvre, *Bull. Soc. chim.*, 1891, [iii], **6**, 415), prepared from 2:3:5-trinitroanisole by the action of methylamine in alcoholic solution (Blanksma, *Rec. trav. chim.*, 1904, **23**, 112), and of which the constitution has been determined by van Romburgh (*Compt. rend.*, 1891, **113**, 505). The formation of this dinitromethylaminoanisole thus gives additional evidence of the constitution of the trinitroanisidine. The lines of evidence which may be now considered as having definitely established the constitution of the trinitroanisidine of m. p. 127—128°* are summarised in the subjoined scheme:

* The method of preparing this trinitroanisidine has been improved by one of the authors (F. R.) so as to enable a yield of 60 per cent. to be obtained, and the



3:5-Dinitro-2-phenoxy-p-anisidine was prepared by heating the trinitroanisidine with four parts by weight of phenol on the water-bath for one hour. After removing the excess of phenol by boiling water and crystallising the residue from alcohol, the above compound was obtained in red, prismatic needles, melting at 178—179°. The substance crystallises also from benzene in small, orange prisms or brown scales:

0.1556 gave 0.2930 CO_2 and 0.0540 H_2O . $\text{C}=51.35$; $\text{H}=3.85$.

0.1254 „ 15.8 c.c. N_2 (moist) at 19.5° and 718 mm. $\text{N}=13.56$.

$\text{C}_{13}\text{H}_{11}\text{O}_6\text{N}_3$ requires $\text{C}=51.14$; $\text{H}=3.61$; $\text{N}=13.77$ per cent.

By these syntheses the mobility of the nitro-group in 2:3:5-trinitroanisidine is definitely established.*

Constitution of Trinitroaminophenol and the corresponding Trinitroanisidine of m. p. 138—139°.

The constitution of the above compounds as 2:3:6-trinitro-derivatives is settled indirectly by the foregoing proof of the constitution of the isomeride, since only two modifications are theoretically possible. Further evidence of a more direct character has, however, been obtained by a careful comparison of the trinitrophenol obtained from the trinitroaminophenol by the diazo-method (T., 1909, **95**, 1382) with known compounds of similar composition. The trinitrophenol in question was originally obtained (*loc. cit.*) in yellow needles melting at 119—120°, and, in view of the evidence thus obtained, was regarded as the unknown 2:3:5-trinitrophenol. The compound approaching this most closely in melting point is the γ -trinitrophenol of Henriques (*Annalen*, 1882, **215**, 332), who assigns to this modification, now known to be the quantity required for the present research was prepared by this method in the laboratory of the University of Geneva by M. M. Bosshard, to whom we desire to express our thanks. The further study of this compound and its derivatives will be continued at Geneva.

* 2:3:6-Trinitro-p-acetylaminophenol also gives phenylic ethers with phenols and phenoxides. The study of these compounds will be continued.

2:3:6-trinitro-compound (Beilstein, II, 692), the m. p. 117—118°. Attempts to prepare a supply of this compound by the original method of Henriques gave very unsatisfactory results in the way of yield, owing to the difficulty of preparing the required 2:3- and 2:5-dinitrophenols by the nitration of *m*-nitrophenol (Bantlin, *Ber.*, 1875, **8**, 21; 1878, **11**, 2104). It was found, however, that the 2:3-dinitro-*p*-aminophenol described in a former paper (T., 1907, **91**, 1481) gave 2:3-dinitrophenol in practically quantitative yield when the diazonium sulphate prepared from this compound in the usual way was boiled with absolute alcohol. The dinitrophenol thus obtained was nitrated in the way described by Henriques, the product converted into barium salt, the latter extracted with alcohol, and the trinitrophenol recovered from the purified barium salt by decomposing the latter with hydrochloric acid. The trinitrophenol thus obtained had the same melting point (119—120°) as that prepared from trinitroaminophenol by the diazo-reaction, and a mixture of the two products had the same melting point. The naphthalene compounds of the two preparations also had the same melting point (100—101°), and a mixture caused no change of melting point. As this trinitrophenol has the nitro-groups in the positions 2:3:6, the trinitroaminophenol and corresponding trinitroanisidine must now be assigned to the same series.

2:3:5-Trinitro-*p*-acetylaminophenol and Derivatives.

A critical study of the products of nitration of diacetyl-*p*-aminophenol under various conditions has led to the conclusions stated in the introductory portion of this paper.* The positions 2:3:5 for the three nitro-groups having been proved for the trinitroanisidine of m. p. 127—128°, it seemed likely that the corresponding trinitroaminophenol or its acetyl derivative would be formed by the further nitration of 3:5-dinitro-*p*-acetyl-(or diacetyl-)aminophenol. A systematic series of experiments with the mono- and di-acetylated 3:5-dinitro-*p*-aminophenol has led to the discovery

* The apparent production of 2:3:6-trinitro-*p*-acetylaminophenol from 3:5-dinitro-*p*-acetylaminophenol has been traced to the presence of 3-nitro-*p*-acetylaminophenol in the compound nitrated. In nitrating diacetyl-*p*-aminophenol so as to produce the 3:5-dinitro-compound, a fuming nitric acid of the highest concentration is required, otherwise some mononitro-compound is formed, and this, on nitration with nitrosulphuric acid, gives the 2:3:6-trinitro-compound. The 3:5-dinitro-compound required for the present research was prepared by the extreme nitration of dibenzoyl-*p*-aminophenol, hydrolysis of the product by sulphuric acid, and subsequent acetylation of the purified 3:5-dinitro-*p*-aminophenol. This process has been found to give more satisfactory results than the direct nitration of diacetyl-*p*-aminophenol.

of the 2:3:5-trinitro-*p*-acetylaminophenol. This last compound is formed when the monoacetyl derivative is nitrated at a low temperature (0°) with fuming nitric acid or when the diacetyl derivative is nitrated at 0° with a mixture of nitric and sulphuric acids. As the process is not easy to carry out successfully, the following details are given:

A mixture of equal volumes of fuming nitric and concentrated sulphuric acid is cooled to 0° , and the diacetyl compound dissolved in the mixture as rapidly as possible in the proportion of 1 gram per 8 c.c. After remaining for about ten minutes, the solution is poured on to ice, and the precipitate, which slowly settles out, is collected and washed with water. It is better to nitrate in batches not exceeding two grams, as with increase of scale the difficulties arising from under-nitration or over-nitration become exaggerated. If allowed to remain too long, so that over-nitration takes place, the whole product is destroyed. The ice used for diluting the solution of the finished product must also be reduced to a minimum, otherwise serious loss occurs through the solubility of the compound in water.

The product obtained as above required several crystallisations from glacial acetic acid before the analytical results indicated that purity had been reached. The pure compound has a decomposing point of $191\text{--}193^{\circ}$, and crystallises in pale, ochreous, lustrous scales. It dissolves freely in alcohol or acetic acid, and to a considerable extent in boiling water, the solution in the latter case being probably accompanied by hydrolysis (de-acetylation). It is phenolic in character, and dissolves in cold sodium carbonate solution. The compound tends to retain acetic acid, and requires drying at 110° in order to give satisfactory results on analysis:

0.1048 gave 0.1280 CO_2 and 0.0212 H_2O . $\text{C}=33.31$; $\text{H}=2.25$.

0.1001 „ 0.1227 CO_2 „ 0.0190 H_2O . $\text{C}=33.43$; $\text{H}=2.11$.

0.0933 „ 16 c.c. N_2 (moist) at 21° and 763.4 mm. $\text{N}=19.61$.

$\text{C}_8\text{H}_6\text{O}_8\text{N}_4$ requires $\text{C}=33.55$; $\text{H}=2.11$; $\text{N}=19.58$ per cent.

The investigation of this trinitro-compound is not yet completed, and a further study will be necessary in order to determine the position of the mobile nitro-group. Its constitution is established by the fact that the trinitroanisidine prepared by methylating the silver salt of the trinitroacetylaminophenol and hydrolysing the product is identical with the 2:3:5-trinitroanisidine of m. p. $127\text{--}128^{\circ}$. The acetyl derivative of the two compounds (m. p. 242°) is also the same.

We desire in conclusion to express our cordial thanks to Mr. Wm. F. Hollely for valuable assistance rendered throughout the

whole course of the research. Mr. R. O. Bishop has also rendered useful service in carrying out many of the analyses. Our thanks to M. Bosshard, which we have pleasure in repeating, have already been recorded in connexion with his special contributions to the experimental work.

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CLX.—*Non-aromatic Diazonium Salts. Part II.*
Azo-derivatives from Antipyrinediazonium Salts
and Their Absorption Spectra.

By GILBERT T. MORGAN and JOSEPH REILLY.

I.—*Antipyrineazo- β -diketo-derivatives.*

1-Phenyl-2:3-dimethylpyrazolone-4-diazonium chloride, which contains its diazo-complex attached to a non-aromatic ring, couples readily with the β -diketones and β -keto-esters, giving rise to well-defined, yellow, crystalline condensation products. With β -diketo-derivatives containing the group $-\text{CO}\cdot\text{CH}_2\cdot\text{CO}-$ or $-\text{CO}\cdot\text{CH}\cdot\text{C}(\text{OH})<$, namely, acetylacetone, benzoylacetone, and ethyl acetoacetate, the condensation involves simply the replacement of one methylene or methenyl hydrogen atom by the diazo-complex, whereas in the case of methyl acetyl ethyl ketone (acetyl-methylacetone), $\text{CH}_3\cdot\text{CO}\cdot\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{CH}_3$, the coupling involves hydrolysis of an acetyl group, so that the product is derived from either methyl ethyl ketone or dimethyl diketone, according as to whether the substance is regarded respectively as an azo-compound or a hydrazone (this vol., p. 811).

An examination of the absorption spectra of these condensation products was made in absolute alcohol, using a Hilger one-prism spectrometer with an iron arc as source of light. In each case the observation was repeated after the addition to the solution of a molecular proportion of sodium ethoxide. The formation of alkali derivative was manifested by a marked deepening of the colour, which was apparent in every case, even in $N/5000$ -solutions.

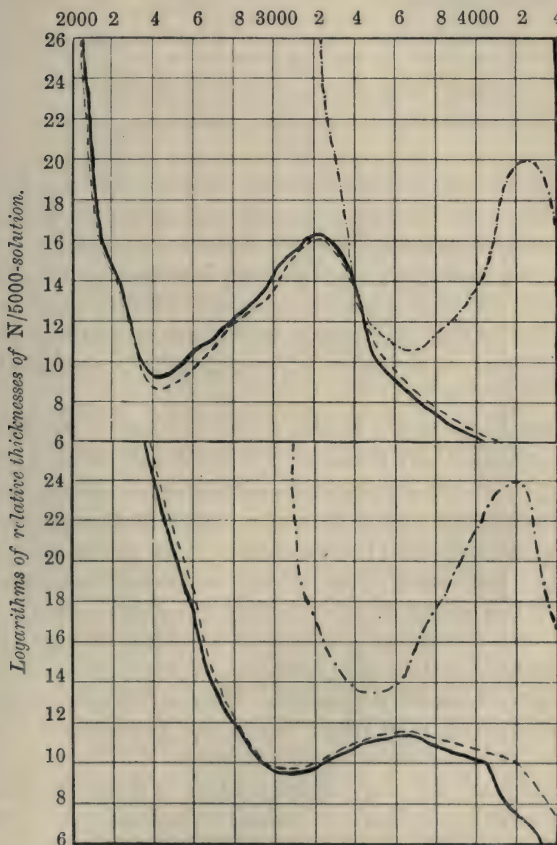
1-Phenyl-2:3-dimethylpyrazolone-4-azoacetylacetone is practically insoluble in water, but dissolves on the addition of a moderate excess ($1\frac{1}{2}$ mols.) of sodium hydroxide. The sodium derivative crystallises from the concentrated solution in orange-brown plates,

decomposing at 215—220°; the same compound separates on evaporating to a small bulk the alcoholic solution of the azo-derivative and sodium ethoxide.

In spite of the very appreciable darkening of the yellow alcoholic

FIG. 1.

— *Acetylacetone.*
 ————— *Antipyrine-4-azoacetylacetone.*
 - - - - - " " " " *sodium derivative.*

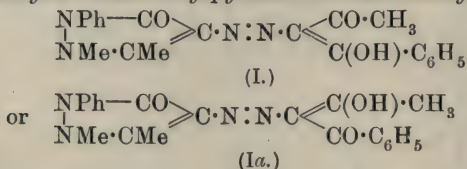


— *Acetylmethylacetone-*
 ————— *Antipyrine-4-azoethyl methyl ketone.*
 - - - - - " " " " *sodium derivative.*

solution of 1-phenyl-2:3-dimethylpyrazolone-4-azoacetylacetone produced by the addition of alkali, its ultra-violet absorption spectrum is almost identical with that of its sodium derivative, the extinction curves (Fig. 1, upper curves) being practically coincident. These

curves are contrasted in the figure with the curve of the parent ketone, and it is seen that the effect of the azo-coupling is to shift very considerably towards the red the characteristic band of acetylacetone itself, the head of the band changing from $1/\lambda$ 3700 to $1/\lambda$ 2450. A similar comparison has been made with benzoylacetone and the corresponding azo-derivative.

1-Phenyl-2:3-dimethylpyrazolone-4-azobenzoylacetone,



A solution of antipyrinediazonium chloride (1 mol.), prepared by diazotising 4-aminoantipyrine hydrochloride in dilute hydrochloric acid solution, was freed from excess of nitrous acid with carbamide, and added to an alcoholic solution of benzoylacetone (1 mol.). The addition of aqueous sodium acetate produced immediately a bulky, yellow precipitate, which was crystallised repeatedly from alcohol, when it separated in bright yellow, rectangular plates, melting at 142—143°:

0.1561 gave 20.4 c.c. N_2 at 20.5° and 761 mm. $\text{N}=14.97$.

$\text{C}_{21}\text{H}_{20}\text{O}_3\text{N}_4$ requires $\text{N}=14.89$ per cent.

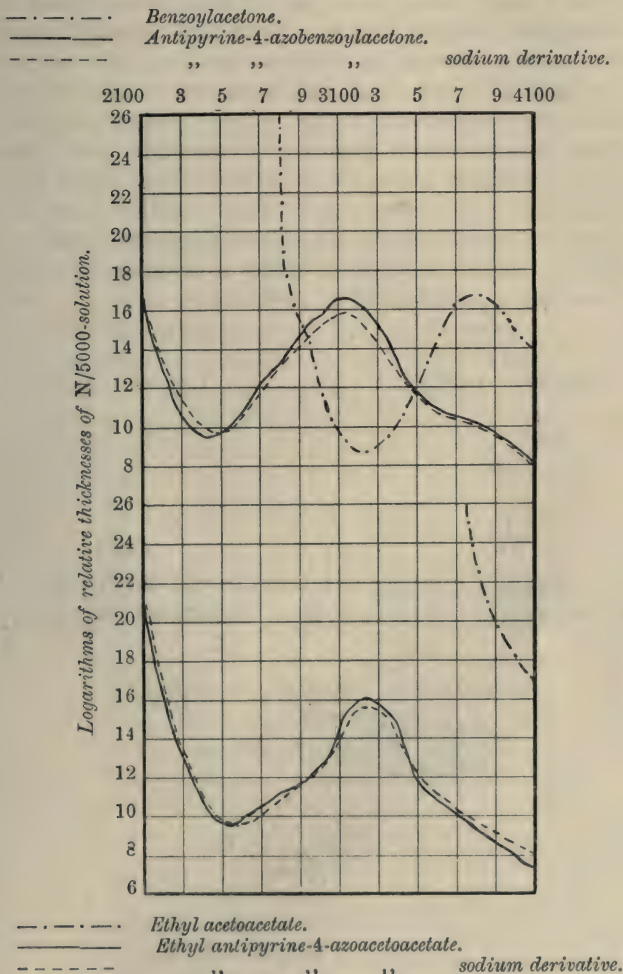
1-Phenyl-2:3-dimethylpyrazolone-4-azobenzoylacetone, which had a more intense yellow colour than the corresponding azo-derivatives of acetylacetone and ethyl acetoacetate, was practically insoluble in water, light petroleum, or ether, but dissolved readily in alcohol, benzene, and the other organic media, being extremely soluble in chloroform or pyridine. Alkali hydroxides change this azo-compound either in the dry state or in alcoholic solution to a bright orange-red alkali derivative. Ferric chloride added to an alcoholic solution of this alkali derivative produced a darkening of the colour even at considerable dilution.

As in the case of the corresponding azo-acetylacetone, the extinction curves of 1-phenyl-2:3-dimethylpyrazolone-4-azobenzoylacetone and its sodium derivative are practically coincident, and they differ from the curve of benzoylacetone in showing the very considerable shift towards the red consequent on the azo-coupling (Fig. 2, upper curves). In other respects the curves of benzoylacetone and its azo-derivative are very similar and practically superposable.

As the foregoing azo-derivatives of acetylacetone and benzoylacetone exhibited ultra-violet absorption spectra very similar to

those of the parent β -diketones and their co-ordinated metallic derivatives (compare Morgan and Moss, this vol., pp. 89, 90), it became of interest to examine the absorption spectrum of ethyl 1-phenyl-2:3-dimethylpyrazolone-4-azoacetoacetate, inasmuch as in

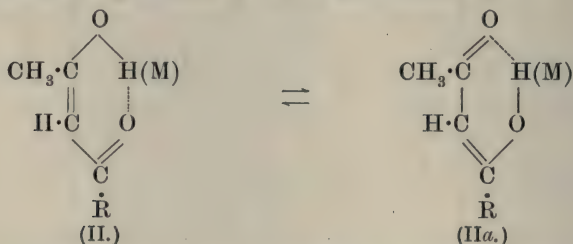
FIG 2.



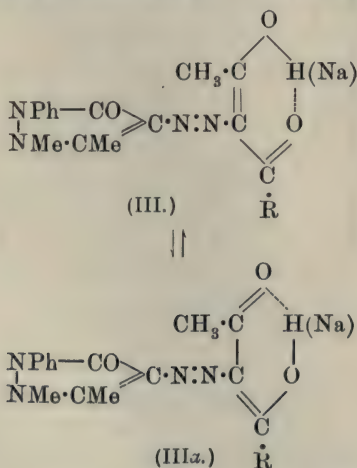
this case the generator, ethyl acetoacetate, shows no selective absorption (Baly and Desch, T., 1904, **85**, 1033). The results (Fig. 2, lower curves) indicate that this azo-compound and its sodium derivative have practically the same ultra-violet absorption,

the extinction curves are coincident, and show the well-defined, persistent band which characterises this group of azo-derivatives.

This spectroscopic evidence supports the view that these antipyrineazo-derivatives of acetylacetone, benzoylacetone, and ethyl acetoacetate have the same enolic constitution as the β -diketones themselves. Moreover, the ultra-violet absorption of these β -diketones is very similar to those of their co-ordinated metallic derivatives (for example, the vanadium and vanadyl compounds, this vol., p. 89). It seems therefore justifiable to assume that, like their metallic derivatives, the β -diketones, the antipyrineazo- β -diketo-compounds, including ethyl antipyrineazoacetoacetate, and the sodium derivatives of these azo-compounds also possess the co-ordination complex (compare Hantzsch, *Ber.*, 1910, **83**, 3053). In the case of the β -diketones and their metallic derivatives, this condition may be expressed by the following general formulæ, where R=methyl or phenyl, and M is either a univalent metallic atom or the chemical equivalent of a multivalent metal:



The co-ordination complex developed in the three antipyrineazo- β -diketo-compounds and their sodium derivatives may be similarly

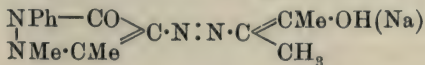


expressed by the general formulæ (III and IIIa), in which R may be either methyl, phenyl, or ethoxyl, corresponding respectively with the azo-derivative of acetylacetone, benzoylacetone (formulæ I and Ia) or ethyl acetoacetate:

The oscillation of the double linkings and the residual affinity ("auxiliary valency") in each of the two foregoing pairs of formulæ is analogous to the rhythmical alternation of the three double linkings assumed by Kekulé in the case of benzene. This conception of the constitution of the antipyrineazo-derivatives of the β -diketo-compounds brings the hypotheses of desmotropy and isorropesis (Baly and Stewart, T., 1906, **89**, 498, 502) into line with the general theory of internally co-ordinated compounds (Werner, *Ber.*, 1908, **41**, 1062), and is, moreover, not incompatible with the views expressed by Lowry and Southgate (T., 1910, **97**, 919) in regard to the part played by residual affinity in determining the selective absorption exhibited by the β -diketones and their derivatives.

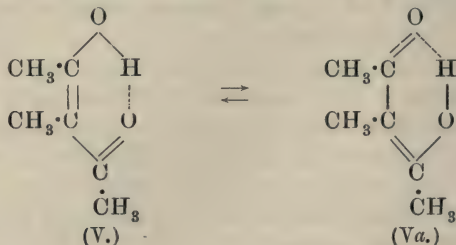
If the foregoing conception of the constitution of these azo-compounds and their sodium derivatives is accepted, then it follows that the presence of the characteristic persistent absorption band in their ultra-violet absorption spectra is an indication of the existence in the molecule of the above indicated co-ordination complex. When the development of this cyclic structure is no longer possible, then the absorption band should either disappear or become very considerably modified. This anticipation is realised by a spectroscopic study of the product obtained by coupling antipyrinediazonium chloride and methyl acetyl ethyl ketone (acetyl methyl acetone). The compound, a pale yellow substance resembling antipyrineazoacetylacetone, differs from this azo-derivative in being quite insoluble in aqueous sodium hydroxide. The pale yellow colour of its alcoholic solution is, however, intensified considerably by the addition of sodium ethoxide (1 mol.), the change being very marked even at a dilution of $N/5000$.

The extinction curves of this compound and its more intensely coloured sodium derivative are practically coincident, and they exhibit a very shallow band (Fig. 1, lower curves). The compound, 1-phenyl-2:3-dimethylpyrazolone-4-azoethyl methyl ketone, and its sodium derivative, may be regarded as having, in alcoholic solution, the enolic configuration (formula IV), from which a six-membered internally co-ordinated ring cannot be developed:



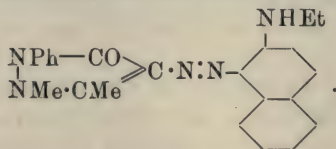
(IV.)

although this structure was probably present in acetylmethylacetone before the elimination of the acetyl group:



II.—Antipyrineazo- β -naphthylamine Derivatives.

1-Phenyl-2:3-dimethylpyrazolone-4-azoethyl- β -naphthylamine,



A solution of antipyrinediazonium chloride, freed from nitrous acid by carbamide, was added to ethyl- β -naphthylamine (O. Fischer, *Ber.*, 1893, **26**, 193) dissolved in alcohol, when a copious precipitate of the sparingly soluble, dark blue hydrochloride of the aminoazo-derivative was immediately produced. The aminoazo-base, freed from its salt by aqueous sodium acetate, was crystallised repeatedly from methyl alcohol, in which it was readily soluble; it separated in red, crystalline plates, sintering at 184° , and melting at 186° :

0.1144 gave 18.0 c.c. N_2 at 20.5° and 761 mm. $\text{N}=18.22$.

$\text{C}_{23}\text{H}_{23}\text{ON}_5$ requires $\text{N}=18.18$ per cent.

This aminoazo-base was very sparingly soluble in water or ether, fairly so in benzene, and dissolving readily in alcohol or pyridine.

1-Phenyl-2:3-dimethylpyrazolone-4-azoethyl- β -naphthylamine hydrochloride, obtained by adding concentrated hydrochloric acid to a solution of the purified base in glacial acetic acid, separated in small, dark blue crystals having a bronzy reflex. This salt, which was only very sparingly soluble in the volatile organic solvents, was prepared for analysis by adding hydrochloric acid (3 mols.) to the purified base, and drying to a constant weight in the vacuum desiccator over solid potassium hydroxide:

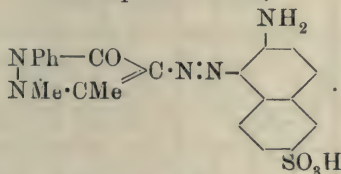
0.0735 gave 0.0255 AgCl . $\text{Cl}=8.58$.

$\text{C}_{23}\text{H}_{24}\text{ON}_5\text{Cl}$ requires $\text{Cl}=8.42$ per cent.

The hydrochloride decomposed indefinitely at 135—140°, and when boiled for some time with alcohol or benzene its colour gradually changed from blue to red. This change is probably due to incipient dissociation, as it is prevented by a slight excess of acid.

The aminoazo-base furnishes deep blue salts even with organic acids, such as acetic acid, and in these compounds it functions as a mono-acidic base. A higher degree of salt-forming power is, however, manifested on treating the blue salts with concentrated sulphuric or hydrochloric acid, when the blue colour is destroyed, giving rise to a purple-red solution. The blue salts are regenerated on diluting this solution with water or alcohol.

1-Phenyl-2:3-dimethylpyrazolone-4-(1')-azo-β-naphthylamine-6'-sulphonic Acid,



β-Naphthylamine-6-sulphonic acid (Brönner acid = 1 mol.) was dissolved in the requisite amount of aqueous sodium carbonate, reprecipitated by excess of dilute acetic acid in a finely divided condition, and the suspension added to an aqueous solution of antipyrine-4-diazonium chloride, which had been previously freed by carbamide from any excess of nitrous acid. A deep blue coloration was developed, and the dark blue hydrochloride of the azo-derivative slowly separated. The precipitate was kept in a vacuum desiccator over alkali hydroxide to remove excess of acid and the reddish-orange azo-derivative set free by aqueous ammonium acetate. This substance was purified by repeated crystallisation from aqueous alcohol, in which it is somewhat soluble; it separated in lustrous, reddish-brown radial aggregates:

0.1174 gave 16.1 c.c. N_2 at 20° and 762 mm. $N = 15.91$.

$C_{21}H_{19}O_4N_5S$ requires $N = 16.02$ per cent.

This azo-sulphonic acid possesses amphoteric properties in a very marked degree. The presence of the sulphonic group permits of the existence of soluble yellow alkali and even ammonium salts, whilst the basic character of the pyrazolone ring renders possible the formation of intensely coloured dark blue salts with mineral or organic acids. Even the sparingly soluble acetate is stable in aqueous solution, and can be crystallised from warm water containing a slight excess of acetic acid. On this account all excess

sociation; the same change occurs in pyridine. The blue colour is restored by the addition of a few drops of acid.

*Absorption Spectra.**—The ultra-violet absorption spectrum of 1-phenyl-2:3-dimethylpyrazolone-4-azo- β -naphthylamine is indicated by the extinction curve in Fig. 3 (upper curves), in which two bands are present, a shallow band towards the violet end, and a persistent band towards the red.

1-Phenyl-2:3-dimethylpyrazolone-4-azoethyl- β -naphthylamine shows very similar selective absorption also with two bands (Fig. 3, lower curves), the one towards the violet end being more persistent than in the case of the azo- β -naphthylamine compound. Sulphonation of the latter substance produces a greater change than ethylation, and in the extinction curve of the azo-derivative of Brönner acid the more refrangible band is reduced to a point of inflection (Fig. 3, lower curves). In each of these three cases the conversion of the aminoazo-compound into its dark blue hydrochloride brings about the same change in the character of the selective absorption. The less refrangible band is rendered more persistent, and where the second band exists (in the unsulphonated compounds) it is reduced to a step out. In addition, the photographic plates indicate in each case the existence of a new narrow band in the visible region which is not shown in Fig. 3. Since even the azo- β -naphthylamine-6-sulphonic acid furnishes a stable hydrochloride, it is very probable that the hydrogen chloride is attracted to the basic nitrogen of the pyrazolone ring rather than to the amino-group of the naphthalene complex, but it is not possible from the available evidence to decide whether or not the marked colour change produced in passing from the aminoazo-compound to its hydrochloride is due to a quinonoid re-arrangement of the aromatic nucleus involving the azo-group. Similar colour changes have already been observed among the Janus azo-dyes which also contain a strongly basic group associated with the azochromophore (Badische Anilin- & Soda-Fabrik, Eng. Pat. 4543/1891 and 18769/1893).

The authors desire to express their thanks to the Research Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

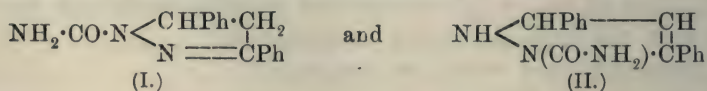
ROYAL COLLEGE OF SCIENCE FOR IRELAND,
DUBLIN.

* The azo- β -naphthylamine derivatives were compared spectroscopically with β -naphthylamine and 4-aminoantipyrine hydrochloride, the solutions being made in absolute alcohol, with the exception of the azo- β -naphthylamine-6-sulphonic acid and its hydrochloride, which, on account of sparing solubility, were examined in alcohol containing 10 per cent. of water.

CLXI.—*Contributions to Our Knowledge of Semicarbazones. Part III. Action of Heat on the Semicarbazones of Phenyl Styryl Ketone and the Preparation of the Corresponding Phenylsemicarbazones.*

By ISIDOR MORRIS HEILBRON and FORSYTH JAMES WILSON.

In a former paper (T., 1912, **101**, 1482) the results of an investigation on the action of semicarbazide on phenyl styryl ketone were communicated. The behaviour of these semicarbazones on heating has now been investigated in the hope of obtaining further insight into their configuration. In this, however, we have been disappointed, as both the α - and β -semicarbazones yield the same products, a transformation of the one stereoisomeride into the other evidently taking place at the elevated temperature required to keep the semicarbazones in the molten condition. During the reaction ammonia was copiously evolved, and on examining the product obtained it was found to consist almost entirely of a substance melting at 189° , together with a very small quantity of another compound melting at 231 — 232° ; the latter substance was unfortunately never obtained in sufficient quantity to permit of further investigation. An analysis and a molecular-weight determination of the substance melting at 189° led to the molecular formula $C_{16}H_{15}ON_3$, identical with that of the semicarbazones themselves. In chemical properties, however, it is entirely different, being incapable of hydrolysis by acid, and thus evidently not a semicarbazone, but is apparently of an analogous type to the compound obtained by the action of heat on the α - or β -semicarbazone of mesityl oxide (Wilson and Heilbron, this vol., p. 377). Like that compound, this substance is exceptionally stable and evidently basic in character, yielding a characteristic picrate, and we assume therefore the substance $C_{16}H_{15}ON_3$ is cyclic in structure, either of the following two formulæ being possible:



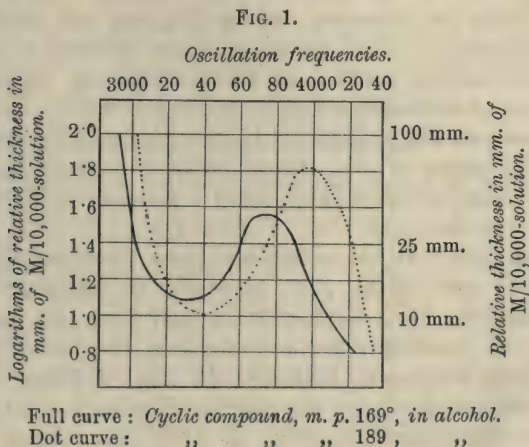
Formula I represents the compound as a pyrazoline derivative, but as we failed to obtain Knorr's pyrazoline reaction, and as the compound, contrary to the characteristic pyrazolines, is exceedingly stable, we are inclined in the meantime to accept formula II as the more likely, this being in agreement with the

conclusion arrived at by Rupe and Kessler (*Ber.*, 1909, **42**, 4503) regarding the cyclic compound from mesityl oxide semicarbazone.

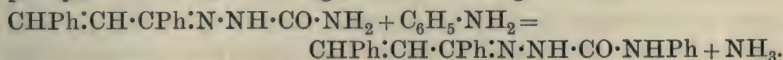
Phenylsemicarbazones of Phenyl Styryl Ketone.

Owing to the interesting phototropic properties exhibited by the semicarbazones of phenyl styryl ketone, it appeared to us of interest to inquire further whether such light phenomena would be met with in other similar derivatives of this ketone, and, as the phenylsemicarbazones could be directly obtained from the parent semicarbazones, they were investigated with somewhat unexpected results.

The method first tried was to heat the semicarbazone with aniline

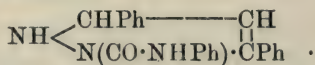


for one hour, which we considered would produce the required phenyl derivative, according to the following reaction:



It was found, however, that with this treatment both the α - and the β -semicarbazone yielded the same products, namely, *s*-diphenylcarbamide and a substance melting at 169°. This compound possessed the same molecular formula, $\text{C}_{22}\text{H}_{19}\text{ON}_3$, as the phenylsemicarbazones, but, as will be made evident, it could not have the structure of a phenylsemicarbazone, and was apparently a cyclic compound of great stability, probably corresponding with the cyclic substance obtained by direct heating of the parent semicarbazones. Although unable definitely to prove this point, further support to this assumption is afforded by a comparison of the absorption spectra of this compound with that of the substance

melting at 189° . As will be seen from the curves shown in Fig. 1, both substances possess very similar absorption curves, and we suggest, in consequence of this, the following formula for this compound melting at 169° :



Having failed to obtain the required phenylsemicarbazones by the previous method, we next tried the effect of heating with aniline for half an hour. Again both semicarbazones reacted similarly, yielding a smaller quantity of *s*-diphenylcarbamide and a white phenylsemicarbazone melting at 184° , the properties of which will be more fully discussed below. A third experiment was now made, in which the semicarbazones were heated with aniline for only five minutes, and in this case each semicarbazone reacted differently. The α -semicarbazone yielded a new white phenylsemicarbazone, melting at 193° , whilst the γ -semicarbazone produced the phenylsemicarbazone melting at 184° .

That these two compounds are indeed phenylsemicarbazones was confirmed by means of their direct preparation from phenyl styryl ketone and phenylsemicarbazide, when a mixture of the two stereoisomerides was obtained.

From the fact that the α -semicarbazone produced the phenylsemicarbazone melting at 193° , it would be expected that they should possess the same configuration, and that this is so is confirmed by the spectrographic examination, the absorption curve of this latter substance indicated in Fig. 2 being practically identical with the curve for the α -semicarbazone (*loc. cit.*, p. 1483). The phenylsemicarbazone melting at 184° possesses, as shown in Fig. 3, a characteristic absorption band, differing in this respect from its stereoisomeride, but quite similar to the absorption curve previously obtained for the γ -semicarbazone, and hence has the same configuration as that compound. According to our previous nomenclature, we designate these two phenylsemicarbazones as α (m. p. 193°) and γ (m. p. 184°).

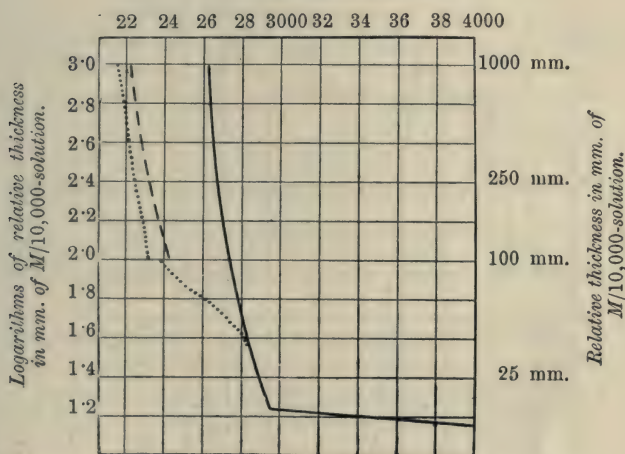
Like the original semicarbazones, alcoholic solutions of the phenyl derivatives are intensely yellow in presence of sodium ethoxide, the intensity of the colour increasing with the quantity of ethoxide present. This fact is clearly indicated in the graphs shown in Figs. 2 and 3, and further, it will be noted that Beer's law does not hold in the ethoxide solutions, but that similar deviations occur, as was found with the semicarbazones themselves (*loc. cit.*). With the introduction of the new phenyl group into the molecule, the phototropic properties of the compounds are greatly increased, for whilst the α -semicarbazone is non-phototropic, the α -phenyl-

semicarbazone is intensely so, becoming deep yellow in the course of a few hours at the ordinary temperature in diffused sunlight, whilst at 100° the change takes place within an hour. In solvents, this phenylsemicarbazone shows pronounced thermotropic properties, the colourless solutions formed in the cold becoming intensely yellow on heating, the depth of colour depending on the temperature attainable in the solvent, all becoming colourless again on cooling.

The same properties are shown by the γ -phenylsemicarbazone, although not to such a pronounced degree. We account for these

FIG. 2.

Oscillation frequencies.

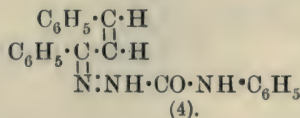
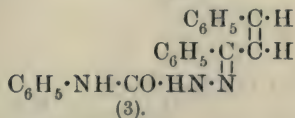
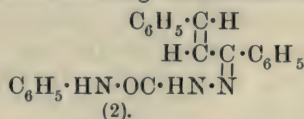
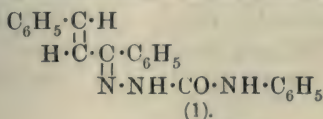


Full curve: Phenylsemicarbazone (m. p. 193°) in alcohol.

Dash " : " " " " " + 10 mol. NaOEt.

Dot " : " " " " " " + 200 " NaOEt.

phenomena in the same way as previously in the case of the parent semicarbazones, suggesting as the most probable explanation that the differences are due to a combination of carbon and nitrogen stereoisomerism, which would allow of the following four isomerides:

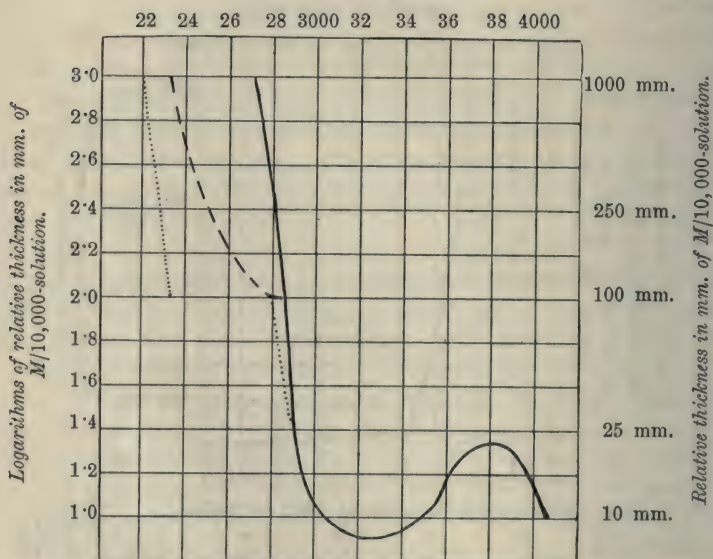


In the present state of our knowledge we do not feel justified in ascribing definitely any one of these formulæ to any particular phenylsemicarbazone, but for the meantime the configurations previously suggested (*loc. cit.*) may be still adopted. We hope, however, to be able shortly to settle this question definitely, and with this end in view we are at present engaged with an investigation on the semicarbazones of methylenedioxyethyl methyl ketone (piperonylideneacetone), which ketone itself is obtainable in two stereoisomeric forms.

The effect of sodium ethoxide on the α - and γ -phenylsemi-

FIG. 3.

Oscillation frequencies.

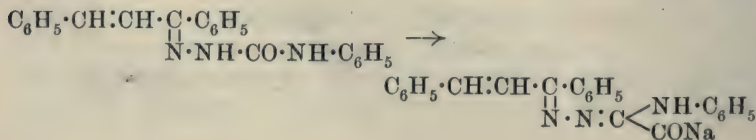


Full curve: Phenylsemicarbazone (m. p. 184°) in alcohol.

Dash " : " " " " " +10 mol. NaOEt.

Dot " : " " " " " +200 " NaOEt.

carbazones respectively is quite similar to that in the case of the original semicarbazones, and we are convinced that the colour produced cannot be satisfactorily accounted for by any alteration in structure due to salt formation. The possibility of salt formation arising from change of structure according to the following formulæ:



cannot be considered, for we have found with semicarbazones derived from saturated ketones, such as acetophenone, no displacement of the absorption curve towards the red end of the spectrum takes place on addition of sodium ethoxide.

We suggest, therefore, as previously, that the effect of the alkali is quite similar to that of light or heat on the phenylsemicarbazones, the α -compound producing the yellow δ -stereoisomeride, the γ -compound changing to the β -stereoisomeride, the amount of either of the yellow forms present depending on the quantity of ethoxide, as can be deduced from the absorption curves. Further, it follows that the equilibrium mixture of the white and yellow stereoisomerides depends not only on the quantity of sodium ethoxide present, but also on the concentration, as is evident from the great deviations from Beer's law.

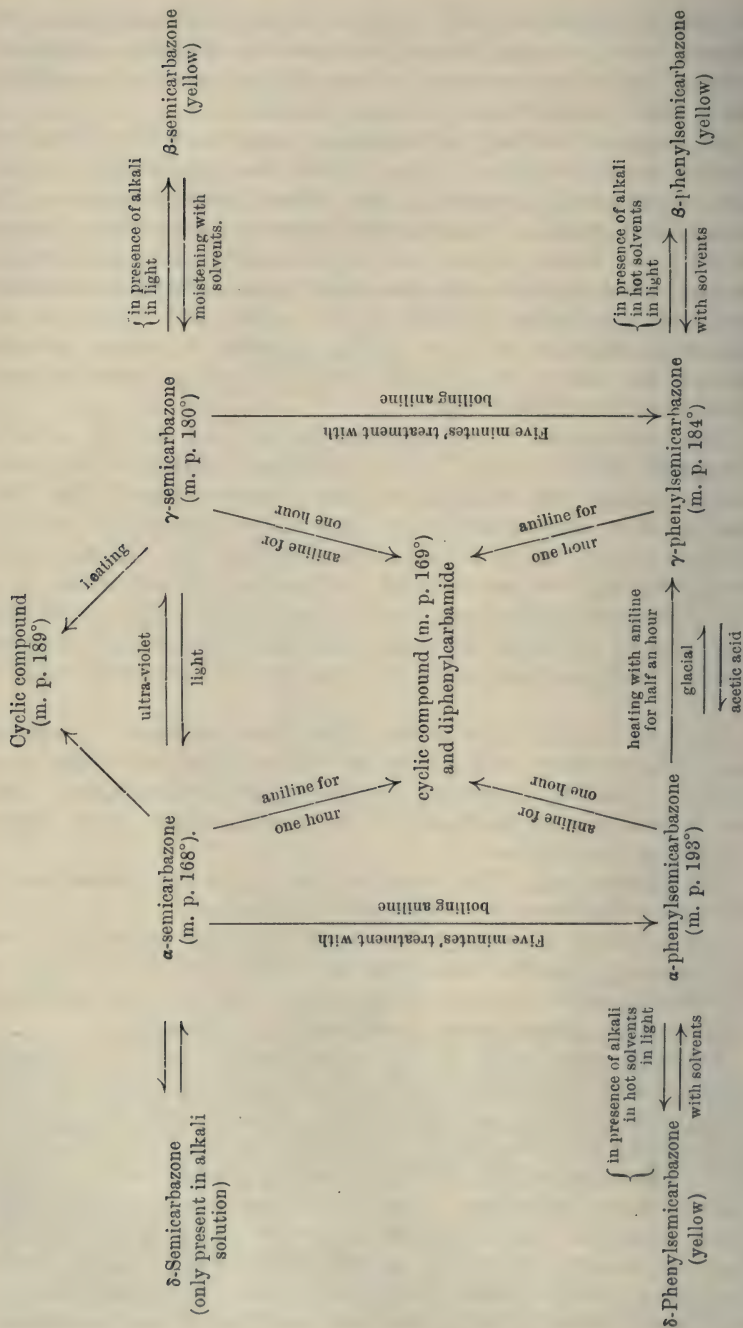
The production of *s*-diphenylcarbamide and of the isomeric compound melting at 169° by the prolonged heating of the parent semicarbazones with aniline, and the non-formation of these substances when the semicarbazones were boiled with aniline for only a short period, led us to the conclusion that this isomeric cyclic compound ought to be obtained by treatment of either the α - or the γ -phenylsemicarbazones with boiling aniline. This prediction was actually confirmed by experiment, both phenylsemicarbazones yielding *s*-diphenylcarbamide and the cyclic compound melting at 169° .

Further, the production of the γ -phenylsemicarbazone, on heating the α -semicarbazone with aniline for half an hour, could only have resulted from the conversion of the α -phenylsemicarbazone, since this is produced on treatment of the α -semicarbazone with boiling aniline in five minutes.

The table on page 1510 illustrates the various transformations of the semicarbazones and the phenylsemicarbazones.

The formation of *s*-diphenylcarbamide can only be accounted for by assuming a partial decomposition of the phenylsemicarbazones on heating, and in support of this there is the fact that prolonged heating with aniline causes considerable resinification.

Attempts were made to hydrolyse the α - and γ -phenylsemicarbazones by the ordinary methods, but under no conditions could phenyl styryl ketone be regenerated. Heating with 20 per cent. hydrochloric acid resulted in both cases in the formation of the cyclic substance melting at 169° . Boiling glacial acetic acid was next tried as a hydrolysing agent; the γ -phenylsemicarbazone under these conditions was converted to a very small extent into the α -stereoisomeride, whilst this α -phenylsemicarbazone under similar conditions passed almost completely into the γ -derivative, an equilibrium evidently being established in favour of the γ -compound.



These actions are apparently dependent on the acid nature of the reagent, and not on the elevated temperature, since heating the γ -phenylsemicarbazone in boiling naphthalene for more than two hours produced no change.

EXPERIMENTAL.

Action of Heat on the α - and γ -Semicarbazones.

Each semicarbazone was heated at 200° for five hours, much ammonia being evolved. The dark-coloured product was allowed to cool, extracted with hot benzene, and the insoluble residue repeatedly crystallised from alcohol. It was thus obtained in white leaflets, melting at 189° . With the exception of hot alcohol and chloroform, the compound is sparingly soluble in all solvents; it is very stable, not being affected by boiling acids or alkalis:

0.1857 gave 0.4908 CO_2 and 0.0988 H_2O . $\text{C}=72.08$; $\text{H}=5.91$.

0.2027 „ 27.2 c.c. N_2 at 17.5° and 761 mm. $\text{N}=15.78$.

0.167, in 15.5 of chloroform, gave $\text{E}=0.155$. $\text{M.W.}=254$.

0.318, „ 15.5 „ „ „ $\text{E}=0.27$. $\text{M.W.}=278$.

$\text{C}_{16}\text{H}_{15}\text{ON}_3$ requires $\text{C}=72.46$; $\text{H}=5.66$; $\text{N}=15.85$ per cent.
 $\text{M.W.}=265$.

These results indicate that the substance is undoubtedly isomeric with the semicarbazones.

The benzene extract, on concentration, yielded a minute quantity of a substance which, on recrystallisation from alcohol, was obtained in needles melting at 230 — 231° . Unfortunately the quantity of the substance was too small to permit of further investigation.

Picrate of Cyclic Compound Melting at 189° .

The picrate was prepared by mixing the substance, dissolved in alcohol, with picric acid dissolved in the same solvent. The precipitate was recrystallised from alcohol, and was obtained in long, golden-yellow needles, melting at 154 — 155° :

0.1870 gave 26.9 c.c. N_2 at 15° and 769 mm. $\text{N}=17.08$.

$\text{C}_{16}\text{H}_{15}\text{ON}_3, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ requires $\text{N}=17.00$ per cent.

Action of Boiling Aniline on the α - and γ -Semicarbazones.

Each semicarbazone was boiled with aniline (5 c.c. of aniline per gram of semicarbazone) for one hour; the product was then poured into dilute acetic acid, and allowed to remain until the oily product became solid. This was then collected, dried, and extracted with boiling benzene. An insoluble residue remained, which, after recrystallisation from alcohol, melted at 237° . This proved to be *s*-diphenylcarbamide, as was confirmed by analysis

and a mixed melting-point test. (Found, C=73·51; H=5·94; N=13·1. $C_{13}H_{12}ON_2$ requires C=73·58; H=5·65; N=13·2 per cent.)

The benzene extract was evaporated to dryness, and the black residue repeatedly recrystallised, first from ethyl acetate, and finally from a mixture of methyl alcohol and benzene. In this way a substance melting at 169° was obtained in long, colourless, transparent prisms, readily soluble in chloroform or benzene, but sparingly so in hot methyl alcohol:

0·1984 gave 0·5610 CO_2 and 0·1022 H_2O . C=77·10; H=5·72.

0·1859 „ 19·6 c.c. N_2 at 17° and 760 mm. N=12·3.

0·3657, in 15·8 chloroform, gave E=0·310. M.W.=290.

0·4267, „ 15·8 „ „ E=0·350. M.W.=300.

$C_{22}H_{19}ON_3$ requires C=77·42; H=5·58; N=12·3 per cent.
M.W.=341.

Like the cyclic compound melting at 189° , this substance proved exceptionally stable, not being acted on by concentrated hydrochloric acid or boiling alkalis.

Having failed in this way to obtain a phenylsemicarbazone, the experiment was repeated under similar conditions, the heating this time being limited to half an hour. The product was worked up as previously described, *s*-diphenylcarbamide being obtained as a residue insoluble in benzene. The benzene extract, on evaporation, left a dark-coloured product, which was recrystallised repeatedly from benzene and petroleum. In this way, white, soft, silky crystals, melting at 184° , were obtained:

0·1845 gave 18·8 c.c. N_2 at 13° and 766 mm. N=12·3.

$C_{22}H_{19}ON_3$ requires N=12·3 per cent.

From the analysis it can be concluded that the substance is a phenylsemicarbazone (γ -modification) of phenyl styryl ketone.

As under these conditions we obtained only one phenylsemicarbazone, the two semicarbazones were again treated with boiling aniline, but this time only for five minutes, when each semicarbazone was found to yield a different phenylsemicarbazone.

α -Semicarbazone with Boiling Aniline for Five Minutes.—The product was poured into dilute acetic acid, and kept in ice for two days, after which the solid mass was collected, dried, and extracted with hot benzene. This treatment dissolved the whole product, no *s*-diphenylcarbamide having been produced in this case. The benzene solution was evaporated, and the residue first crystallised from ethyl acetate, and then from a mixture of chloroform and light petroleum, when colourless needles, melting at 193° , were obtained:

0.1847 gave 19.6 c.c. N_2 at 12° and 740 mm. $N=12.4$.

$C_{22}H_{19}ON_3$ requires $N=12.3$ per cent.

The analysis shows that this substance is a phenylsemicarbazone (α -modification) of phenyl styryl ketone.

γ -Semicarbazone with Boiling Aniline for Five Minutes.—The reaction product was worked up as before, and yielded wholly the γ -phenylsemicarbazone, no *s*-diphenylcarbamide being formed.

Direct Preparation of the α - and γ -Phenylsemicarbazones from Phenyl Styryl Ketone.

Molecular quantities of phenyl styryl ketone dissolved in alcohol, phenylsemicarbazide hydrochloride dissolved in water, and potassium acetate dissolved in alcohol, were mixed, sufficient water being added to dissolve the potassium chloride formed. After twenty-four hours the precipitate was collected and recrystallised from ethyl acetate, crystals of the α -phenylsemicarbazone being obtained. The mother liquors, on dilution with water, yielded a further precipitate, which, on recrystallisation from a mixture of chloroform and light petroleum, yielded the γ -phenylsemicarbazone. It is worthy of note that on many occasions the two phenylsemicarbazones were precipitated together, and form apparently various mixtures of constant melting point, from which it is exceedingly difficult to isolate either form, as the solubility of the two stereoisomerides in all solvents is practically identical. By means of carbon disulphide, from which the two phenylsemicarbazones were deposited in different crystalline forms, it was possible to isolate the two constituents mechanically.

Properties of the Phenylsemicarbazones.

α -Phenylsemicarbazone.—This modification, unlike the original α -semicarbazone, is extremely phototropic, being rapidly converted by light into an intensely yellow stereoisomeride (δ -modification), which, on recrystallisation from all solvents, is reconverted into the white α -form. The rate of transformation of the α - into the δ -form is accelerated by rise of temperature. Both forms, however, possess the same melting point.

In solution, the α -modification possesses thermotropic properties, the solution on heating becoming yellow, and colourless again on cooling; probably an equilibrium mixture of the α - and δ -forms exists in solution at temperatures above the ordinary.

γ -Phenylsemicarbazone.—In properties this modification is very similar to the α -phenylsemicarbazone. It is converted by light,

although not so readily, into a yellow stereoisomeride (β -form) of the same melting point; the thermotropic properties in solution were very faint.

Action of Aniline on the α - and γ -Phenylsemicarbazones.

Each phenylsemicarbazone was boiled with aniline (5 c.c. of aniline per gram of substance) for one hour, ammonia being evolved during the reaction. On working up the product as previously described, there was obtained, as was to be expected, besides *s*-diphenylcarbamide, the cyclic substance melting at 169° .

Action of Acids on the α - and γ -Phenylsemicarbazones.

(a) *Hydrochloric Acid*.—Each phenylsemicarbazone was heated with 25 per cent. hydrochloric acid on a sand-bath for half an hour. On cooling, the oily mass produced gradually solidified, and was recrystallised from alcohol, which deposited crystals of the cyclic substance, melting at 169° .

(b) *Acetic Acid*.

α -Phenylsemicarbazone.—The phenylsemicarbazone was gently boiled with glacial acetic acid for two hours. On addition of water, a precipitate formed, which, on recrystallisation from carbon disulphide, yielded the γ -modification almost exclusively, only a small quantity of the original α -form remaining.

γ -Phenylsemicarbazone.—The reaction was carried out in the same way; the product consisted chiefly of unaltered γ -form, but a small quantity of the α -phenylsemicarbazone was isolated.

It is evident from this reaction that acetic acid, like aniline (compare p. 1512), favours the formation of the γ -phenylsemicarbazone.

In conclusion, we desire to express our thanks to the Carnegie Trust for the Universities of Scotland for a grant which has defrayed the expenses of this investigation.

CHEMISTRY DEPARTMENT,
ROYAL TECHNICAL COLLEGE, GLASGOW.

CLXII.—*The Ten Stereoisomeric Tetrahydroquinaldinomethylenecamphors.*

By WILLIAM JACKSON POPE and JOHN READ.

THE ease with which *d*-oxymethylenecamphor undergoes condensation with primary and secondary amines renders available a simple method for ascertaining whether such amines are externally compensated or potentially optically inactive; an externally compensated amine yields two stereoisomeric condensation products with *d*-oxymethylenecamphor, whilst a potentially inactive base yields but one such derivative (Pope and Read, T., 1909, **95**, 171). The discovery of a method by means of which the amine can be recovered in quantitative yield from the condensation product with *d*-oxymethylenecamphor (Pope and Read, T., 1912, **101**, 2325) furnishes an obviously convenient process for resolving externally compensated bases of the kind referred to into their optically active components. We have successfully applied this process to the resolution of several externally compensated amines; but in one case, that of *dl*-tetrahydroquinaldine, have found that the resolution with the aid of the condensation with *d*-oxymethylenecamphor presents unexpected difficulties; the investigation of these difficulties has led to a number of interesting results, which are described in the present paper.

As is well known, the Pasteur method for resolving externally compensated bases, which consists in crystallising them with an optically active acid and isolating the two possible salts, *dBdA* and *lBdA*, by fractional crystallisation, quite frequently fails. Ladenburg showed (*Annalen*, 1909, **364**, 227) that two such salts are occasionally capable of forming a double compound, *dAlB,2dA*, which he termed a partially racemic compound; it is probably now generally realised that the cases of failure of this particular Pasteur method are, in general, due to the production of such partially racemic compounds.

Although numerous instances of the formation of partially racemic compounds have been investigated, all hitherto recognised have been cases in which the additive compound, *dAlB,2dA*, has been formed between two salts; since electrolytically dissociable substances appear particularly prone to form compounds of the nature of double salts, it was expected that the method of resolving externally compensated bases by the aid of their condensation products with *d*-oxymethylenecamphor would not be liable to hindrance by the occurrence of this complication. During the

present investigation it was, however, found that externally compensated tetrahydroquinaldine cannot be resolved by crystallisation of its condensation product with an equivalent quantity of *d*-oxymethylenecamphor, and further study showed that the optically inactive base forms a partially racemic compound with the *d*-camphor derivative; an entirely new type of partially racemic compound, in which the two components are not electrolytes, has thus been discovered. At the same time, it has been found possible to resolve *dl*-tetrahydroquinaldine by means of *d*-oxymethylenecamphor by taking advantage of the fact that the two enantiomorphously related tetrahydroquinaldines condense with *d*-oxymethylenecamphor at very different rates.

Since both *d*- and *l*-tetrahydroquinaldine can now be readily obtained in quantity by a method which we have previously described (T., 1910, **97**, 2199), and *d*- and *l*-oxymethylenecamphor are also available, we have been able to prepare all the possible optically active, partially racemic and wholly racemic stereoisomeric tetrahydroquinaldinomethylenecamphors; these latter are ten in number, and are listed in the following table in order of decreasing solubility. The symbol *d* or *l* indicates the sign of the tetrahydroquinaldyl residue, and *D* or *L* that of the methylenecamphor radicle:

		M. p.
1. <i>d</i> - <i>D</i> }	Wholly uncompensated active compounds	81.0°
2. <i>l</i> - <i>L</i> }		
3. <i>l</i> - <i>D</i> , <i>l</i> - <i>L</i> }	Partially racemic compounds	83.5
4. <i>d</i> - <i>D</i> , <i>d</i> - <i>L</i> }		
5. <i>l</i> - <i>D</i> }	Partially internally compensated compounds ...	111.5
6. <i>d</i> - <i>L</i> }		
7. <i>l</i> - <i>D</i> , <i>d</i> - <i>D</i> }	Partially racemic compounds	113.0
8. <i>l</i> - <i>L</i> , <i>d</i> - <i>L</i> }		
9. <i>d</i> - <i>D</i> , <i>l</i> - <i>L</i> }	Fully racemic compounds	126.5
10. <i>d</i> - <i>L</i> , <i>l</i> - <i>D</i> }		
		135.5

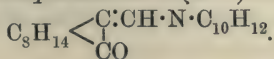
The above table shows that the solubility of the isomeric substances diminishes as the melting point rises; this is a point of some interest as indicating a relationship between the melting points of these substances, which may be regarded as constitutionally identical, and the ease with which they are liquefied by a solvent.

Method of Preparation.

The tetrahydroquinaldinomethylenecamphors are all prepared by mixing warm solutions in ethyl alcohol and 50 per cent. acetic acid of the oxymethylenecamphor and the tetrahydroquinaldine respectively; a sudden separation of an oily product occurs after a few seconds, and, after a short time, the mixture is poured into water and the oil extracted with light petroleum. The petroleum solution is then repeatedly shaken with dilute hydrochloric acid

and with dilute sodium hydroxide solution in order to remove uncondensed base or oxymethylenecamphor; this treatment is essential, and if neglected the crystallisation of the product is either hindered or entirely prevented. After a final extraction with dilute alkali, the petroleum solution is caused to crystallise by evaporation, and the product recrystallised from light petroleum; the yield of the final pure product is about 80 per cent. of the theoretical.

d-(or *l*)-Tetrahydroquinaldino-*d*-(or *l*)-methylenecamphor,



The petroleum solutions of these two enantiomorphously related, wholly uncompensated, optically active substances, obtained as above described, can only be caused to crystallise with extreme difficulty. After thorough repeated extractions with acid and alkali, a little of the concentrated solution is made to crystallise by rubbing on a watch-glass with concentrated sodium hydroxide solution; the crystalline material thus obtained is used to inoculate the main bulk of solution. The compounds are very soluble in most organic solvents, even in light petroleum, and crystallise in white, feathery needles, melting at 81° . It is interesting to note that a crystalline nucleus of the one substance induces the crystallisation of a supersaturated solution of the enantiomorphously related isomeride:

0.1042 of *d*-*D* compound gave 0.3106 CO_2 and 0.0816 H_2O .
 $\text{C}=81.29$; $\text{H}=8.76$.

$\text{C}_{21}\text{H}_{27}\text{ON}$ requires $\text{C}=81.49$; $\text{H}=8.80$ per cent.

The following determinations of the rotation constants of *d*-tetrahydroquinaldino-*d*-methylenecamphor, like all the rotatory power determinations stated in the present paper, were made at 20° in 4-dcm. tubes, the quantities of substance named being made up to 30 c.c. with the solvent. The light used is indicated by the wave-length, namely, $\text{Hg}_{\text{violet}}=4359$, $\text{Hg}_{\text{green}}=5461$, $\text{Hg}_{\text{yellow}}=5780$, $\text{Na}_{\text{yellow}}=5893$. The foregoing particulars refer also to all the determinations of rotatory power stated in the present paper:

	0.1114 gram in ethyl alcohol.			0.5020 gram in ethyl alcohol.		
	Hg, 5461.	Hg, 5780.	Na, 5893.	Hg, 5461.	Hg, 5780.	Na, 5893.
α	-2.71°	-2.15°	-1.98°	-12.16°	-9.60°	-8.88°
$[\alpha]$	-183	-145	-133	-182	-143	-133
$[\text{M}]$	-564	-447	-412	-561	-443	-410
Rotatory dispersions: Hg, 5461/Na, 5893=1.361; Hg, 5780/Na, 5893=1.086						
Hg, 5461/Na, 5893=1.369; Hg, 5780/Na, 5893=1.081.						

	0.1052 gram in glacial acetic acid.			0.5009 gram in glacial acetic acid.		
	Hg, 5461.	Hg, 5780.	Na, 5893.	Hg, 5461.	Hg, 5780.	Na, 5893.
α	-1.91°	-1.47°	-1.34°	-13.06°	-10.24°	-9.51°
$[\alpha]$	-136	-105	-95.5	-196	-153	-142
$[M]$	-421	-324	-295	-604	-474	-440
Rotatory dispersions: 1.425; 1.097.			1.373; 1.077.			

The acetic acid solutions exhibit marked mutarotation; the first of the above solutions gave for Hg, 5461 the following values of α : after 30 minutes, -2.54° ; 1.5 hours, -2.00° ; 2.5 hours, -1.91° ; 48 hours, -1.91° . The second solution gave: after 1 hour, -13.18° ; 1.5 hours, -13.08° ; 2.5 hours, -13.06° ; 14 hours, -13.06° . The values given in the tables were obtained after the rotatory power had become constant:

	0.1003 gram, <i>d</i> -Tetrahydroquin- aldino- <i>d</i> -methylenecamphor, in ethyl alcohol. Hg, 4359.	0.1108 gram <i>l</i> -Tetrahydroquin- aldino- <i>l</i> -methylenecamphor in ethyl alcohol. Hg, 5461. Hg, 5780. Na, 5893.
α	-8.00°	+2.69° +2.13° +1.98°
$[\alpha]$	-598	+182 +144 +134
$[M]$	-1848	+563 +446 +414
Hg, 4359/Na, 5893 = 4.488.		1.359; 1.076.

In all the solvents used, *d*-tetrahydroquinaldino-*d*-methylenecamphor is strongly lævorotatory; the close numerical agreement between the values for the two enantiomorphously related substances in ethyl alcoholic solution indicates that both compounds were obtained in a state of high purity.

d-(or *l*)-Tetrahydroquinaldino-*l*-(or *d*)-methylenecamphor.

These substances were prepared by the method described above from the corresponding pure optically active tetrahydroquinaldines and oxymethylenecamphors; they separate from light petroleum solutions in large, pale yellow crystals, melting at 111.5° . The isomerides may also be crystallised from aqueous acetone, and are easily soluble in most of the ordinary organic solvents; they readily yield supersaturated solutions, which may be caused to crystallise by inoculation with a crystal of either isomeride:

0.1004 of *l*-*D* compound gave 0.2991 CO_2 and 0.0796 H_2O .
C = 81.25; H = 8.87.

$\text{C}_{21}\text{H}_{27}\text{ON}$ requires C = 81.49; H = 8.80 per cent.

d-Tetrahydroquinaldino-*l*-methylenecamphor gave the following results on determination of the rotation constants:

	0.1030 gram in benzene.			0.5017 gram in ethyl alcohol.		
	Hg, 5461.	Hg, 5780.	Na, 5893.	Hg, 5461.	Hg, 5780.	Na, 5893.
α	-11.03°	-9.16°	-8.61	-63.19°	-52.20°	-49.10
$[\alpha]$	-803	-667	-627	-945	-780	-734
$[M]$	-2482	-2061	-1937	-2919	-2411	-2268
Rotatory dispersions: 1.281; 1.064.			1.287; 1.063.			

0.1535 gram in acetic acid.			
α	-17.77°	-14.63°	-13.74°
$[\alpha]$	-868	-715	-671
$[M]$	-2683	-2209	-2074

Rotatory dispersions: 1.293; 1.065.

The acetic acid solution showed marked mutarotation; after 30 minutes from the time of making up, α was observed as -19.60° ; 1.5 hours, -18.25° ; 2.5 hours, -17.88° ; 6.5 hours, -17.77° . The values given above were obtained after the rotatory power had become constant.

l-Tetrahydroquinaldino-*d*-methylenecamphor gave the following values:

0.1109 gram in ethyl alcohol.				0.5008 gram in ethyl alcohol.		
α	+14.06°	+11.63°	+10.95°	+63.07°	+52.20°	+49.01°
$[\alpha]$	+951	+787	+741	+945	+780	+734
$[M]$	+2938	+2430	+2288	+2919	+2411	+2268

Rotatory dispersions: 1.284; 1.062.

1.287; 1.063.

0.1061 gram in ethyl alcohol.		0.1056 gram in ethyl alcohol.	
Hg, 4359.		Landolt's G, 4482.	
α	+35.64°	+13.70° (2-dcm. tube).	
$[\alpha]$	+2519	+1946	
$[M]$	+7785	+6013	

The rotatory dispersion, $\text{Hg}, 4359/\text{Na}, 5893 = 3.402$; the dispersion constant suggested by Lowry (this vol., p. 1069), namely, $\text{Hg}, 4359/\text{Hg}, 5461 = 2.649$.

So far as we are aware, these two substances exhibit higher specific rotatory powers in solution than do any compounds hitherto described; Werner has recorded (*Ber.*, 1912, **45**, 3066) as the largest observed specific rotation the value $[\alpha] + 1300^\circ$ of potassium *d*-chromoxalate for the Landolt G, 4482 filter. The tetrahydroquinaldine derivatives now described give a specific rotatory power half as large again, namely, 1946° , for the same colour of light; it may be noted that benzoquinone *d*-camphoryl- ψ -semicarbazone has a larger specific rotation for the *D*-line than our compounds (Forster, T., 1905, **87**, 722).

d-Tetrahydroquinaldino-*l*-methylenecamphor and its enantiomorphously related isomeride crystallise on spontaneous evaporation of their light petroleum solutions in lustrous, pale bluish-green tablets which are highly refractive. Mr. A. Hutchinson, M.A., of the Mineralogical Laboratory, Cambridge, has kindly examined the crystals, and the following description is abstracted from his account of the results which he has obtained. The crystals belong to the orthorhombic system, and, in their development, exhibit no signs of enantiomorphous hemihedrism; they may thus be pro-

visionally assigned to the rhombic bipyramidal sub-class, although, in view of the enantiomorphous molecular configuration of the compounds, they may ultimately be placed in the sphenoidally hemihedral class (compare Kipping and Pope, T., 1897, 71, 989). The forms $m\{110\}$ and $q\{101\}$ are dominant, and the crystals are developed tabularly on faces of one or other of these two forms. Inasmuch as no indications of enantiomorphism were observed, the crystals of the two substances appear goniometrically identical.

Axial ratios: $a : b : c = 0.9630 : 1 : 0.7552$.

Forms observed: $b\{010\}$, $c\{001\}$, $m\{110\}$, $o\{011\}$, $d\{021\}$, $q\{101\}$, $p\{111\}$.

The following angular measurements were obtained:

Angle.	<i>l-D.</i>		<i>d-L.</i>		
	No. of measurements.	Observed.	No. of measurements.	Observed.	Calculated.
010 : 011	3	52°54'	—	—	52°56'30"
011 : 021	2	19 19 30"	—	—	19 16
010 : 111	15	59 17	—	—	59 17
111 : 101	15	30 43	3	30°41'	—
110 : 111	22	42 36 30	11	42 39	42 35
001 : 111	20	47 25	7	47 22	—
111 : 011	7	31 57	—	—	32 2
111 : 021	8	36 51 30	—	—	36 52
110 : 011	24	65 17	13	65 19	65 17
011 : 101	24	51 0	16	51 0	51 0
110 : 101	27	63 43	13	63 41	—
110 : 021	8	54 39	2	54 31 30"	54 45
110 : 010	12	46 0	—	—	46 5
110 : $\bar{1}\bar{1}0$	8	87 59	—	—	87 50
001 : 011	3	37 2	—	—	37 3 30
001 : 101	11	38 0	—	—	37 56
101 : 021	4	64 9	—	—	64 4 30
111 : $\bar{1}01$	9	78 2	—	—	77 53
101 : $\bar{1}01$	—	—	3	76 0	75 52
011 : 0 $\bar{1}1$	—	—	6	74 3	74 7

d-(or *l*)-Tetrahydroquinaldino-*dl*-methylenecamphor.

These two enantiomorphously related substances, prepared from pure optically active tetrahydroquinaldine and externally compensated oxymethylenecamphor in the manner described above, separate from light petroleum solution in clusters of long, thin prisms, melting at 83.5°. The same substances are obtained by crystallising equal weights of *d*-(or *l*)-tetrahydroquinaldino-*d*-methylenecamphor and *d*-(or *l*)-tetrahydroquinaldino-*l*-methylenecamphor together from light petroleum solution:

0.1068 of the *d-DL* compound gave 0.3180 CO₂ and 0.0851 H₂O.

C=81.20; H=8.92.

C₂₁H₂₇ON requires C=81.49; H=8.80 per cent.

The following determinations of rotatory power were made with *d*-tetrahydroquinaldino-*dl*-methylenecamphor:

	0.1016 gram in ethyl alcohol.			0.1062 gram in acetic acid.		
	Hg, 5461.	Hg, 5780.	Na, 5893.	Hg, 5461.	Hg, 5780.	Na, 5893.
α	-7.82°	-6.43°	-5.96°	-7.13°	-5.83°	-5.54°
$[\alpha]$	-577	-475	-440	-504	-412	-384
$[M]$	-1784	-1467	-1360	-1556	-1272	-1187
Rotatory dispersions: 1.312; 1.071.				1.310; 1.072.		

The acetic acid solution exhibits mutarotation; the above solution gave the following values for α , 5461: 30 minutes after being made up, -8.15°; 1.5 hours, -7.39°; 2.5 hours, -7.25°; 6.5 hours, -7.20°; 24 hours, -7.13°. The values recorded in the table were obtained after the rotatory power had attained a constant value.

A solution containing 0.1030 gram in ethyl alcohol gave for Hg, 4359, $\alpha = -21.63^\circ$; whence $[\alpha] -1575^\circ$ and $[M] -4867^\circ$. The rotatory dispersion, Hg, 4359/Na, 5893 = 3.580.

The following values were obtained with *l*-tetrahydroquinaldino-*dl*-methylenecamphor:

	0.1006 gram in ethyl alcohol.		
	Hg, 5461.	Hg, 5780.	Na, 5893.
α	+7.70°	+6.32°	+5.95°
$[\alpha]$	+574	+471	+444
$[M]$	+1774	+1456	+1371
Rotatory dispersions: 1.294; 1.062.			

A comparison of the values last stated with those given above for the enantiomorphously related substance under similar conditions shows that the corresponding constants agree very closely; it thus cannot be doubted that the two substances now described represent definite double or partially racemic compounds. This conclusion is supported by the fact that on distilling either substance in a current of steam after addition of concentrated hydrochloric acid, pure externally compensated oxymethylenecamphor is obtained; the pure optically active base can subsequently be recovered by rendering the solution alkaline and continuing the distillation.

The experimental data given above abundantly prove that the two substances under consideration are true partially racemic compounds, and that, in the crystalline condition, they are composed of equal quantities of the two optically active but non-enantiomorphously related components; in view of the unusually large number of stereoisomeric substances of the same constitution which are now described, it seems desirable to consider whether the available evidence points to the occurrence of combination between

the optically active substances in the solutions from which they are deposited. A very sensitive test for such combination is provided by the comparison of the specific rotatory powers of the partially racemic substances and their components; if no combination exists in solution it would be expected that the partially racemic substances should exhibit rotatory powers which are the algebraic mean of those of their components. The values stated in the following table are for the 0.33 per cent. alcoholic solutions:

	$[\alpha]$ for	Hg, 4359.	Hg, 5461.	Hg, 5780.	Na, 5893.
1. <i>d</i> - <i>D</i> (observed)		-598°	-183°	-145°	-133°
2. <i>l</i> - <i>D</i> „		+2519	+951	+787	+741
3. <i>d</i> - <i>LD</i> (calculated)		-1558	-567	-466	-437
4. <i>d</i> - <i>LD</i> (observed)		-1575	-577	-475	-440
5. <i>l</i> - <i>LD</i> „		—	+574	+471	+444
6. <i>dl</i> - <i>D</i> (calculated)		+960	+384	+321	+304
7. <i>dl</i> - <i>D</i> (observed)		—	+391	+326	+307
8. <i>dl</i> - <i>L</i> „		-975	-390	-326	-307

The consideration of the data 1 to 5 in the above table shows that the agreement between the observed and the calculated rotatory powers of the partially racemic substances is so good as to furnish no support for the view that combination exists in the solution between the two components of the partially racemic substance which exists in the crystalline condition as a definite compound.

The two compounds now under consideration crystallise sufficiently well on spontaneous evaporation of the light petroleum solutions to allow of their goniometric examination. Mr. Hutchinson has kindly examined the crystals with the following results. The compounds form prismatic crystals belonging to the sphenoidal sub-class of the monosymmetric system; the crystals are elongated in the direction of the axis of symmetry, and the pinacoids $a\{100\}$ and $c\{001\}$ thus form the long faces of the prisms. The axis-*b* is polar, and the crystals of the two compounds are enantiomorphously related.

Axial ratios: $a:b:c=1.332:1:1.290$; $\beta=74^{\circ}0'$.

Forms present: On *d*-*DL*: $a\{100\}$, $c\{001\}$, $b'\{0\bar{1}0\}$, $\{110\}$, $d\{2\bar{1}0\}$, $o\{0\bar{1}1\}$, $p\{\bar{1}11\}$. On *l*-*Dl*: $a\{100\}$, $c\{001\}$, $m'\{1\bar{1}0\}$, $d'\{210\}$, $o'\{011\}$, $p'\{\bar{1}\bar{1}1\}$.

The following angular measurements were obtained:

Angle.	<i>d</i> -DL.		<i>l</i> -DL.		Calculated.
	No. of measurements.	Observed.	No. of measurements.	Observed.	
100 : 001	19	74° 2'	8	74° 0'	74° 0'
100 : 001	18	106 0	8	106 0	106 0
100 : 110	7	51 52	3	51 45	52 0
001 : 110	6	80 0	2	80 41	80 13
100 : 210	15	32 37	4	32 35	—
001 : 210	14	76 29	5	76 39	76 35
100 : 011	12	80 6	3	80 11	80 2
001 : 011	12	51 7	5	51 10	—
100 : 111	6	66 32	2	66 23	66 14
001 : 111	5	64 14	4	64 11	64 30
110 : 111	7	35 33	—	—	—

In accordance with the results to which Barlow and Pope have arrived concerning the morphotropic relationships existing between the crystalline forms exhibited by substances of similar chemical constitution (T., 1908, **93**, 1528), it is to be anticipated that a close morphotropic relationship should be found between the two pairs of enantiomorphously related substances which are now crystallographically described, namely, *d*-(and *l*)-tetrahydroquinaldino-*l*-(and *d*)-methylenecamphor and *d*-(and *l*)-tetrahydroquinaldino-*dl*-methylenecamphor. The indications of the theory have been followed in detail in connexion with stereoisomerides by Jerusalem (T., 1912, **101**, 1268) with entire success. The goniometric data now recorded do not immediately exhibit the expected morphotropic relationship, but the latter becomes at once evident on transposing the axial ratios of the orthorhombic *d*-(or *l*)-tetrahydroquinaldino-*l*-(or *d*)-methylenecamphor, so that the values, $a : b : c = 0.9630 : 1 : 0.7552$, are stated in the form, $b : c : a = 1.324 : 1 : 1.275$. The axial ratios, stated in this latter form, correspond closely with those for *d*-(or *l*)-tetrahydroquinaldino-*dl*-methylenecamphor, namely, $a : b : c = 1.332 : 1 : 1.290$; $\beta = 74^\circ 0'$; the morphotropic relationship required by the results of Barlow and Pope, which have been traced in so many instances by Jerusalem, is thus to be observed existant between the compounds now described.

dl-Tetrahydroquinaldino-*d*-(or *l*)-methylenecamphor.

This pair of partially racemic compounds is prepared in the manner described above from externally compensated tetrahydroquinaldine and *d*- or *l*-oxymethylenecamphor; both substances crystallise readily from the light petroleum solutions in rosettes composed of pale yellow, glistening prisms, melting at 113° . The substances are purified by recrystallisation from light petroleum, and their constancy of composition was proved by treatment with bromine in carbon tetrachloride solution in the manner previously

described (Pope and Read, T., 1912, 101, 2337); the orange-yellow additive product, when evaporated to dryness in alcoholic solution, yields a mixture of bromoxymethylenecamphor and externally compensated tetrahydroquinaldine hydrobromide. The definite character of the partially racemic compounds was further demonstrated by subjecting them to fractional crystallisation; the successive fractions all exhibited the same rotation constants:

0.1014 of the *dl-D* compound gave 0.3023 CO₂ and 0.0790 H₂O.

C=81.31; H=8.72.

C₂₁H₂₇ON requires C=81.49; H=8.80 per cent.

The rotation constants of the two compounds are given by the following determinations:

0.1066 gram of <i>dl-D</i> in ethyl alcohol.				0.1016 gram of <i>dl-L</i> in ethyl alcohol.			
	Hg, 5461.	Hg, 5780.	Na, 5893.		Hg, 5461.	Hg, 5780.	Na, 5893.
α	+5.56°	+4.63°	+4.37°		-5.28°	-4.41°	-4.16°
$[\alpha]$	+391	+326	+307		-390	-326	-307
$[M]$	+1208	+1007	+949		-1204	-1006	-949
Rotatory dispersions: 1.272; 1.059.				1.269; 1.060.			

0.1018 gram of <i>dl-L</i> in acetic acid.				0.1008 gram of <i>dl-L</i> in ethyl alcohol.	
	Hg, 5461.	Hg, 5780.	Na, 5893.	Hg, 4359.	
α	-5.18°	-4.32°	-4.07°	-13.11°	
$[\alpha]$	-381	-318	-300	-957	
$[M]$	-1179	-984	-927	-3014	
Rotatory dispersions: 1.273; 1.061.				Hg, 4359/Na, 5893=3.176.	

The rotatory powers of these two partially racemic substances can be calculated in the same manner as in the case of *d*-(or *l*)-tetrahydroquinaldino-*dl*-methylenecamphor; the results are stated on p. 1522, numbers 6 to 8 of the table, and lead to conclusions similar to those drawn in connexion with the first pair of partially racemic compounds.

Mutarotation is observed in acetic acid solutions; the values of α obtained for the above acid solution were as follows: after 30 minutes, -5.44°; 1.5 hours, 5.34°; 2.5 hours, -5.26°; 6.5 hours, -5.18°. The full set of data recorded was measured when the rotatory power had become constant.

dl-Tetrahydroquinaldino-dl-methylenecamphor.

This compound is one of the two possible fully racemic isomerides, and is conveniently prepared by crystallising a petroleum solution containing equal quantities of *d*-tetrahydroquinaldino-*d*-methylenecamphor and the enantiomorphously related substance. It forms small, hard, pale yellow, glistening prisms, which melt at 126.5°, and is more soluble than the fully racemic compound next to be

described, although less soluble than either of the eight optically active isomerides dealt with above. The substance shows no tendency to form supersaturated solutions, and is only produced in very small proportion when externally compensated tetrahydroquinaldine and oxymethylenecamphor are caused to condense together; it is conveniently described as the *d-D,l-L* isomeride:

0.1098 gave 0.3292 CO₂ and 0.0873 H₂O. C=81.77; H=8.90.

C₂₁H₂₇ON requires C=81.49; H=8.80 per cent.

dl-Tetrahydroquinaldino-ld-methylenecamphor.

This compound, the least soluble of the ten isomerides now described, is obtained on mixing light petroleum solutions of equal weights of *d*-tetrahydroquinaldino-*l*-methylenecamphor and the enantiomorphously related substance; it forms clusters of soft, glistening plates or needles, which melt at 125.5°, and are free from the pale yellow tint exhibited by all the other isomerides. This substance is produced almost exclusively when pure *dl*-tetrahydroquinaldine is condensed with *dl*-oxymethylenecamphor. It is optically inactive in solution, and shows no tendency to form supersaturated solutions; its method of formation proves it to be the substance *d-L,l-D*:

0.1043 gave 0.3124 CO₂ and 0.0815 H₂O. C=81.69; H=8.74.

C₂₁H₂₇ON requires C=81.49; H=8.80 per cent.

In addition to the two fully racemic compounds, *d-D,l-L* and *d-L,l-D*, described above, it appeared possible that a doubly racemic compound, composed of equal weights of these two substances, might exist. On subjecting a mixture in equal proportion of the two racemic substances to fractional crystallisation from light petroleum solution, the compound *d-L,l-D* is readily isolated in a state of purity as the least soluble constituent, whilst the isomeride *d-D,l-L* is deposited from the final mother liquors. The intermediate fractions show the characteristic crystals of the two fully racemic compounds deposited side by side; there is thus no tendency towards the formation of a doubly racemic compound of the composition *d-D,l-L,d-L,l-D*.

Mixed Crystallisations of the Stereoisomerides.

In view of the large number of double compounds which are formed amongst this group of stereoisomerides, results of some interest were to be expected from the study of the manner in which two of the isomerides can undergo change when crystallised together; the theoretical point involved has not previously been

treated experimentally or discussed, but will be clearly understood from the following considerations.

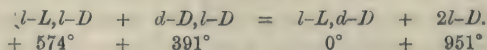
The two partially racemic, and enantiomorphously related, compounds, *d-L,d-D* and *l-L,l-D*, are appreciably more soluble in light petroleum than are the two fully racemic substances, *d-D,l-D* and *d-L,l-L*; further, equivalent proportions of each pair of substances contain the same amounts of each of the four simple optically active components, *d-D*, *l-L*, *d-L*, and *l-D*, and it has also been shown above that the available experimental evidence indicates that the partially racemic, and therefore also the fully racemic, compounds are dissociated in solution. Consequently, on crystallising a mixture of equal weights of the two partially racemic substances, the solution should deposit the more sparingly soluble isomerides, namely, the pure fully racemic substances. This is actually what occurs: on crystallising together equal weights of the two partially racemic, enantiomorphously related compounds from light petroleum, the two fully racemic substances are deposited, and are readily separated in the manner already noted (p. 1525).

Every possible sort of case, in which the final equilibrium established in the heterogeneous system of liquid and solid is conditioned by the solubilities of the several crystalline stereoisomerides, is embraced by the following series of experiments.

(a) On crystallising together equal quantities of the two partly racemic compounds, *d-L,d-D* and *l-L,l-D*, the fully racemic substances, *d-L,l-D* and *d-D,l-L*, are deposited.

(b) On crystallising together equal quantities of the other two enantiomorphously related partially racemic compounds, *d-D,l-D* and *d-L,l-L*, the fully racemic substances, *d-L,l-D* and *d-D,l-L*, also separate. In the study of cases (a) and (b) the conclusions stated were confirmed by the observation that all the fractions of substance which separated were optically inactive in solution.

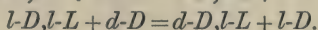
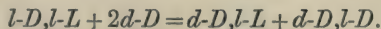
(c) On crystallising together equal quantities of two partially racemic, but not enantiomorphously related, substances, namely, the substances *l-L,l-D* and *d-D,l-D*, the first separation exhibited $[\alpha]_{5461} = +350^\circ$ in ethyl alcohol; on recrystallisation, this value fell to $+128^\circ$, when the fractionation of this deposit was abandoned. The mother liquors deposited the large crystals characteristic of the substance *l-D*, and these, on further crystallisation, gave the value $[\alpha]_{5461} = +948^\circ$. The change which had been effected may be represented by the following equation, in which the substances dissolved are stated on the left, the substances produced on the right:



The remarkable result is thus arrived at that, by crystallising two partially racemic compounds together, one of the optically active components can be separated in a state of purity together with the fully racemic compound.

(d) On crystallising together equal quantities of two partly racemic, but not enantiomorphously related substances, the pair of substances being so selected as not to be enantiomorphously related to the pair dealt with under (c), no sharp separation of the crystalline products was found easily possible. The isomerides used were the *l-L,l-D* and *d-L,l-L*, and the first separation gave $[\alpha]_{5461} = -164^\circ$; this value was but slightly changed on recrystallisation, and corresponds with a mixture of about three parts of *d-L,l-L* with one part of *l-L,l-D*. As the end which it was desired to attain, namely, the production of a pure optically active substance by the crystallisation of a mixture of partly racemic compounds, had been achieved as described under (c), this more difficult case was not further studied.

It is interesting to note that on crystallising together a mixture of one of the more soluble partially racemic compounds with one pure optically active substance, a fully racemic compound should be deposited together with another partially racemic substance or a pure optically active component, according to the proportion in which the mixture is made up. Thus, the following changes would be expected:



The amount of material at our disposal was insufficient to permit of the full investigation of the changes thus indicated, but the experiments which we were able to make indicated that the equations given actually represent the changes which take place.

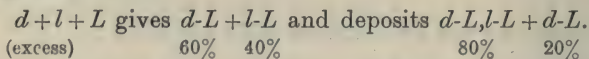
Resolution of dl-Tetrahydroquinaldine by d-Oxymethylenecamphor.

Since the two substances, *d-D* and *l-D*, form a definite partially racemic compound, it might be expected that externally compensated tetrahydroquinaldine could not be resolved by condensation with *d*-oxymethylenecamphor; the compound *d-D,l-D* cannot be separated into its components by recrystallisation. The resolution referred to can, however, be brought about readily by treating a considerable excess of the externally compensated base with *d*- or *l*-oxymethylenecamphor.

The possibility of the resolution is due to a very unusual kind of cause. It has been already indicated that the condensation of *dl*-tetrahydroquinaldine with *dl*-oxymethylenecamphor leads to the production almost exclusively of the fully racemic substance *d-L,l-D*,

very little of the other fully racemic compound, *d-D,l-L*, being formed. This shows that the optically active condensation product, *d-L*, is produced much more readily than is the stereoisomeride, *d-D*. When therefore *d*-oxymethylenecamphor is placed together with a large excess of *dl*-tetrahydroquinaldine under the conditions favourable to condensation, most of the former substance is used up in the production of the substance *l-D*, whilst the smaller proportion serves to yield the product *d-D*; on fractional crystallisation some of the partially racemic compound, *d-D,l-D*, first separates, and the substance *l-D* may subsequently be separated from the mother liquors. On treating *dl*-tetrahydroquinaldine (2.5 molecular proportions) with *l*-oxymethylenecamphor (1 molecule) in the usual manner, and separating the uncondensed base by distillation with steam after rendering the mixture alkaline, tetrahydroquinaldine giving the value $[\alpha]_{5461} = -12.2^\circ$, resulted. Calculation from this number shows that of the base which had reacted, 60.8 per cent. was of the dextro- and 39.2 per cent. was of the lævo-configuration. On extracting the crude condensation product and allowing the petroleum solution to crystallise, practically the whole of the component *l-L* is deposited as the partially racemic compound *d-L,l-L*; the component *d-L* is then caused to separate in an almost pure condition by inoculating the mother liquor.

The mechanism of the resolution may be expressed by the following equation:



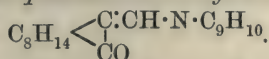
It is very remarkable that a reaction of the type of this condensation, which proceeds almost as rapidly as an ionic interaction, should yield the two products, *l-L* and *d-L*, with such very different velocities. The separation thus outlined is effected easily and almost quantitatively, and the pure optically active base is readily obtained from the final product by hydrolysis of the resulting *d*-tetrahydroquinaldino-*l*-methylenecamphor with strong hydrochloric acid in the manner described above (p. 1521).

The present appears to be the most effective instance yet recorded of the application of the difference between two chemical reaction velocities to the resolution of an externally compensated substance. Such processes as those described by Marckwald and McKenzie (*Ber.*, 1901, **34**, 469) and Marckwald and Meth (*Ber.*, 1905, **38**, 801), which involve partial esterification or amide formation, are necessarily slow, and the isolation of the pure optically active product is a matter of difficulty.

In all these preparations it is essential to use tetrahydroquinaldine, which is so pure that it will crystallise on inoculation

(Pope and Read, T., 1910, **97**, 2199), and oxymethylenecamphor, which is crystalline and has been freshly steam distilled; if this precaution is not taken, a considerable amount of uncrystallisable gummy condensation product is formed. The nature of this latter material is not clear, but analysis shows that it has the same percentage composition as the crystalline condensation products.

Tetrahydroquinolino-d-methylenecamphor,



For purposes of comparison, it was desirable to prepare the condensation products of tetrahydroquinoline with the oxymethylenecamphors; the condensation proceeds readily under the usual conditions, and the product, tetrahydroquinolino-*d*-methylenecamphor, crystallises from light petroleum in large, well-developed, pale yellow prisms, melting at 110°:

0.1104 gave 0.3298 CO₂ and 0.0847 H₂O. C=81.47; H=8.59.

C₂₀H₂₅ON requires C=81.36; H=8.47 per cent.

The following determinations of rotatory power were made:

0.0932 gram in ethyl alcohol.			
	Hg, 5461.	Hg, 5780.	Na, 5893.
α	+8.05°	+6.69°	+6.28°
$[\alpha]$	+648	+538	+505
$[\text{M}]$	+1911	+1588	+1491

Rotatory dispersions: 1.282; 1.065.

Mr. Hutchinson has kindly measured the crystals, and gives the following data concerning them:

Crystal system: Monosymmetric.

$a:b:c=1.4623:1:—$; $\beta=62^\circ 40'$.

Forms observed: $a\{100\}$, $b\{010\}$, $c\{001\}$, $m\{110\}$.

The dominant form is $m\{110\}$, and no form was observed which would enable the calculation of the ratio c/b ; the following angular measurements were made:

Angle.	No. of measurements.	Observed.	Calculated.
100 : 001	10	62°40'	—
100 : 110	19	52 25	—
001 : 110	18	73 44	—
110 : $\bar{1}10$	12	75 4	75°10'

Tetrahydroquinolino-dl-methylenecamphor.

This substance, prepared in the usual manner, separates from light petroleum in large, lustrous prisms, melting at 111°; it is much less soluble than the isomeric compound:

0.1204 gave 0.3595 CO_2 and 0.0921 H_2O . $\text{C}=81.43$; $\text{H}=8.56$.

$\text{C}_{20}\text{H}_{25}\text{ON}$ requires $\text{C}=81.36$; $\text{H}=8.47$ per cent.

All the condensation products of the oxymethylenecamphors with tetrahydroquinoline and the tetrahydroquinaldines described in the present paper are stable towards hot sodium hydroxide solution, but are readily hydrolysed by warm hydrochloric acid. We have previously pointed out (T., 1909, **95**, 175) that the condensation products of other primary and secondary amines with oxymethylenecamphor in general resist hydrolysis with acid. The governing rule appears to be that when the nitrogen atom of the amine forms part of an open chain, the condensation product is stable against hot hydrochloric acid; when the nitrogen atom is in a closed ring, the condensation product is readily hydrolysed. In either case the hydrobromide of the base is easily obtained by titrating the warm alcoholic solution of the condensation product with bromine.

THE CHEMICAL LABORATORY,
UNIVERSITY OF CAMBRIDGE.

CLXIII.—*A New Method of Preparing m-Chlorobenzoic Acid and the Investigation of its Hydroxylamine Salt.*

By WILHELM GLUUD and RICHARD KEMPF.

In former experiments, it was noticed that when benzoic acid was treated with *aqua regia*, a comparatively quiet reaction took place, even at the temperature of the water-bath. It is surprising that the action of this powerful agent under these conditions should be limited to the formation of a mixture of *o*- and *m*-chlorobenzoic acids.

The yield of *m*-chlorobenzoic acid in the crude form is 60 per cent. of the benzoic acid used, and this product is sufficiently pure for many preparations, and certainly for technical purposes. The process described may be preferable in practice to the known methods of preparing *m*-chlorobenzoic acid, although the yield of the purified acid is only about 40 per cent.

The hydroxylamine salt of *m*-chlorobenzoic acid was investigated in the hope of using it in the separation of the acid, as hydroxylamine benzoate is stated (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 380) to be very sparingly soluble in water. This statement proved

to be incorrect. Both salts are fairly soluble in cold water, and very readily so on heating. On evaporating the aqueous solution of hydroxylamine benzoate, the salt undergoes a considerable decomposition into its components, and this may perhaps have given rise to the incorrect statement. When rapidly heated, both salts show a fairly sharp melting—or decomposition—point, especially when freshly prepared. If heated gently, the *m*-chlorobenzoate does not melt, but only sinters violently, leaving a substance which itself melts above 200°. The investigation shows that the hydroxylamine salts, when heated above their melting point, decompose, leaving the ammonium salts of the acids. The formation of hydroxamic acids was not noticed. The aqueous solutions of the ammonium salts very easily give off ammonia on heating. The salts are also readily soluble in some organic solvents on warming, but ammonia is evolved, leaving for the most part only the free acid in solution.

It is evident that ammonium *m*-chlorobenzoate is much more easily decomposed than the benzoate, and this agrees with Hantzsch's observation (*Ber.*, 1907, **40**, 3804).

EXPERIMENTAL.

Twenty grams of benzoic acid were warmed on a water-bath with 400 c.c. of hydrochloric acid (D 1.19), and to the warm solution 65 c.c. of nitric acid (D 1.4) were added in small portions for about twenty minutes. An oil soon collected, which, after remaining for about half an hour on the water-bath with frequent shaking, gradually solidified to a crystalline mass. The crystals were heated for a very short time with about 200 c.c. of water; the mass melted, was allowed to solidify, and then again collected (23 grams). It was then dissolved in 200 c.c. of *N*-sodium hydroxide, and the warm solution poured slowly into a boiling solution of 20 grams of calcium chloride in 300 c.c. of water, the mixture being quickly filtered while hot. The precipitate was washed with water, decomposed with hydrochloric acid, and the product collected and dried (12 grams). The compound melted at about 140°, after considerable sintering at 125°.

One gram was dissolved in 100 c.c. of boiling water, and on filtering the colourless hot solution, 0.7 gram of a substance was obtained, which began to sinter at about 140°, and melted at 150°. The yield was about 40 per cent. of the benzoic acid used. The product contained about 95 per cent. of *m*-chlorobenzoic acid, as shown by a chlorine estimation. The compound may be therefore sufficiently pure to be used for most purposes.

The filtrate containing the soluble calcium salts gave, on acidify-

ing, a substance which melted at 117° after vigorous sintering (7 grams). If once recrystallised from water, the sintering began at 117° , and the mass was entirely melted at 130° . The product was considered to be impure *o*-chlorobenzoic acid.

In order to prepare large quantities of *m*-chlorobenzoic acid from benzoic acid, smaller amounts of concentrated hydrochloric acid can be used. For instance, with 80 grams of benzoic acid and only 700 c.c. of hydrochloric acid, good results are obtained. The vessels used should be of large size on account of frothing.

For comparison, an experiment in which 20 grams of benzoic acid were treated with 400 c.c. of concentrated hydrochloric acid and 80 grams of potassium chlorate, yielded, on decomposing the calcium salt, only 7.3 grams of *m*-chlorobenzoic acid, which was of a deep red colour, and was completely liquid at 120° . After recrystallising from water, a pale grey substance was obtained, which mostly liquefied at 110° , but was completely melted at 130° .

Hydroxylamine Benzoate.

The precipitation of a solution of sodium benzoate with a solution of hydroxylamine hydrochloride gave only a small amount of an impure product. The following method of preparation was therefore adopted.

Benzoic acid (61 grams) was dissolved in a methyl-alcoholic solution of hydroxylamine, and the solution was evaporated in a vacuum. The residue was extracted with chloroform in a Soxhlet apparatus, when large, glistening crystals (42.2 grams) gradually collected in the distillation bulb. This product melted at 121 – 122° to a clear liquid, which gave off bubbles of gas. It dissolved in excess of ether or alcohol in the cold, less readily in hot chloroform or benzene. It was soluble in 15–20 parts of cold water, dissolving readily in the hot solvent.

Effect of Heat on Hydroxylamine Benzoate.

Twenty grams of hydroxylamine benzoate were heated in an oil-bath at 120° , and within about ten minutes the temperature was raised to 180 – 190° . Benzoic acid and other products were evolved. The cooled mass was powdered and treated with ether to remove benzoic acid (4.8 grams), and purified by dissolving 1 gram in cold methyl alcohol, decolorising with charcoal in the cold, and precipitating the salt with excess of ether (0.4 gram). This salt proved to be ammonium benzoate, melting at 197 – 198° .

Hydroxylamine m-Chlorobenzoate.

The salt was prepared by precipitating sodium *m*-chlorobenzoate solution with a concentrated solution of hydroxylamine hydrochloride. The product was collected, and extracted several times with hot xylene. In this way, from 15 grams of red *m*-chlorobenzoic acid, 6 grams of fine needle-shaped crystals separated from the xylene, which, on rapidly heating, melted and decomposed at 145—146° after a short sintering. The product was fairly readily soluble in cold water, but not entirely, as it contained some *m*-chlorobenzoic acid. In warm water it dissolved easily. On heating very slowly, the salt sintered at about 140°, especially if the product was not freshly prepared, forming a viscous, crystalline mass, which melted at 200°. The difference between the freshly prepared salt and that which had been exposed to the air shows that some decomposition into the ammonium salt proceeds apparently even at the ordinary temperature.

Effect of Heat on Hydroxylamine m-Chlorobenzoate.

Three grams of the hydroxylamine salt were placed in an oil-bath at 130°, and the temperature was slowly raised to 170°; much *m*-chlorobenzoic acid was given off. The solidified mass was treated with warm xylene to remove most of the *m*-chlorobenzoic acid, the residue consisting of a mixture (1.5 grams) of ammonium *m*-chlorobenzoate and the acid itself, from which the latter was obtained by treatment with cold water. In order to separate the ammonium salt, the mixture was extracted with warm acetone (boiling should be avoided, as it would cause loss of ammonia), and the ammonium salt precipitated from the acetone solution by means of light petroleum. The salt crystallised in small, iridescent rosettes or leaflets, which melt and decompose at 203—204° after a short sintering. It dissolved readily in cold water, and in some organic solvents on heating, but so readily evolved ammonia that little but the acid itself was left in solution. Even the aqueous solution, on heating, gave off ammonia, and *m*-chlorobenzoic acid crystallised out on cooling. The salt seemed to dissociate into its components more readily than the corresponding benzoate.

Ammonium *m*-chlorobenzoate was also prepared directly by passing ammonia into a methyl-alcoholic solution of *m*-chlorobenzoic acid. By addition of ether, the salt was precipitated in silky, glistening scales, which were identical with the salt previously prepared.

DAVY FARADAY LABORATORY.

CLXIV.—*The Influence of Temperature and Pressure on the Volatility of Zinc and Cadmium.*

By THEKETH KUMARAN NAIR and THOMAS TURNER.

In previous papers on the behaviour of certain alloys when heated in a vacuum (Turner, *J. Inst. Metals*, 1912, **7**, 105; Groves and Turner, *T.*, 1912, **101**, 585) it has been shown that under certain conditions of time and temperature some alloys are quantitatively separated into their constituent metals; others are partly separated, whilst a third class is inseparable. In conducting some experiments on a practical scale, with charges of about 150 kilos., it was found that the rate of volatilisation of zinc from an alloy was diminished to a very considerable extent by imperfections in the vacuum. Thus a pressure of air equal to about one inch of mercury appeared to make distillation at 500° indefinitely slow, and to raise the practical working temperature by fully 200°. As this difference in temperature would be likely to render the process unprofitable, it became of importance to ascertain the manner in which the volatilisation of zinc is affected by variations in the pressure of air or other gases.

EXPERIMENTAL.

The natural suggestion was to determine the vapour pressure, and the partial pressure of zinc vapour, for various temperatures; but as no convenient method is available for such determinations, advantage was taken of an indirect method depending on the loss of weight in a unit of time. This gives a rate of volatilisation which is comparable for various temperatures and pressures. The actual details were as follows.

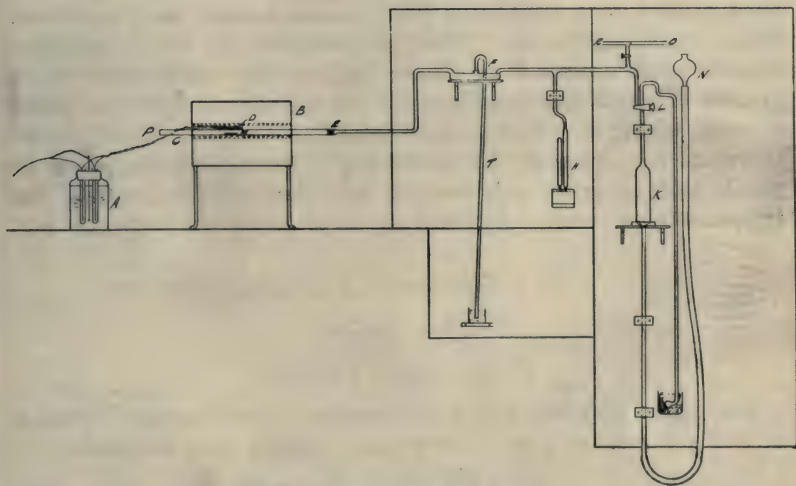
In each experiment one gram of pure zinc was carefully weighed and placed in a porcelain boat. It was then introduced into a porcelain tube, which was arranged so that a horizontal furnace, which was electrically heated, could be slid over it, and removed, when required, in a few seconds. The porcelain tube was connected at one end with a mercury pump, and with a shortened mercury pressure gauge, as described in the papers quoted above. The addition of an extra glass tap permitted of the ready introduction of air or other gases as desired. The temperature of the electric furnace was ascertained by means of a properly calibrated thermocouple (Fig. 1).

It will be noted that *B* is the resistance furnace electrically heated, *C* the porcelain tube, and *M* the porcelain boat containing the weighed quantity of metal. The end of the tube *P* is closed

with a glass lid with sealing-wax joint; *D* is the thermocouple, and *A* the thermo-flask for the cold junction. The end *E* is sealed on to a glass tube by sealing-wax joint; this glass tube is sealed on to the phosphoric oxide drying tube *F*, and is thus in connexion with the barometer tube *T*, the shortened pressure gauge *H*, and the mercury pump *LKN*. An auxiliary pump was attached at *O*, whilst *R* was employed for the introduction of the gases used in the experiments.

The weighed quantity of zinc was introduced through the end of the porcelain tube remote from the pump. This end of the tube was closed with the glass plate and sealing-wax joint. The desired pressure was then obtained, and the electric current passed

FIG. 1.

*Vacuum furnace and pump.*

at such a rate as would ensure the desired temperature being reached in thirty minutes. At first sight this may appear somewhat difficult, but with practice and attention it could be done with considerable regularity. Later experiments showed that the length of time occupied in heating the furnace was relatively unimportant. It was therefore heated as quickly as convenient to a few degrees below the desired point, and the exact temperature obtained by careful adjustment in a few minutes. The temperature was then maintained as nearly as possible constant for exactly thirty minutes, when the furnace was slid away from the tube, and the latter was allowed to cool quickly in the air. As the experiments were conducted on an ascending scale, that is, beginning

with low temperatures and pressures, and gradually working up to higher ones, there is good reason to believe that the volatilisation during the heating up stage was exceedingly small, and that practically the whole loss of weight occurred during the uniform heating period, which in every case lasted for thirty minutes.

A description of the first series of experiments, in which the gas used was dry air, will illustrate the general method of procedure. Starting with a vacuum as complete as could be conveniently obtained, and with a residual pressure which never exceeded 1 mm. of mercury, samples were heated to various temperatures, and the loss of weight in thirty minutes was determined as before described. No attempt was made to ascertain the minimum temperature at which volatilisation commenced, as this has already been partly investigated by Demarçay and others. Such observations would also involve considerable time, and be of little practical value. The temperature at which complete volatilisation occurred in thirty minutes was ascertained by a process of guess and trial, guided by the direction of the curve already obtained. The temperatures for complete volatilisation therefore may possibly be rather high; the error in any case is small, and is quite unimportant for the object in view. The temperature errors are believed to be of about the order of $\pm 5^\circ$.

Experimental Results.

First Series.

I.—Zinc in a Vacuum.

The zinc employed was Mond spelter, and contained upwards of 99·9 per cent. of zinc. The values obtained were as follows:

Temperature	340°	360°	380°	400°	420°	440°	460°
Volatilisation, per cent.	5·52	15·94	27·32	46·98	71·36	89·36	99·9

II.—Zinc in Air. Pressure 3 mm. of mercury.

Temperature	350°	400°	450°	500°
Volatilisation, per cent.	1·16	6·36	49·76	99·9

III.—Zinc in Air. Pressure 20 mm.

Temperature	510°	520°	530°	550°	570°	600°	620°
Volatilisation, per cent.	10·62	21·0	28·0	50·18	70·16	93·61	99·7

IV.—Zinc in Air. Pressure 50 mm.

Temperature	580°	600°	620°	640°	660°	690°
Volatilisation, per cent.	9·78	23·18	41·48	53·52	71·58	99·9

V.—*Zinc in Air. Pressure 80 mm.*

Temperature	640°	660°	680°
Volatilisation, per cent.	46·68	67·66	83·96

VI.—*Zinc in Air. Pressure 200 mm.*

Temperature	650°	700°	720°
Volatilisation, per cent.	22·26	68·66	87·9

VII.—*Zinc in Air. Pressure 600 mm.*

Temperature	770°	800°	840°
Volatilisation, per cent.	31·18	50·84	98·4

Second Series.

In this series the same experimental method was followed. The apparatus was exhausted after the weighed quantity of zinc had been introduced. Purified dry hydrogen was then admitted up to atmospheric pressure; the apparatus was again exhausted, and hydrogen admitted to the required pressure.

I.—*Zinc in Hydrogen. Pressure 20 mm.*

Temperature	520°	550°	600°
Volatilisation, per cent.	28·0	56·46	99·94

II.—*Zinc in Hydrogen. Pressure 50 mm.*

Temperature	560°	580°	600°	620°	640°
Volatilisation, per cent.	16·86	43·28	65·38	78·36	99·9

Third Series.

In these experiments the gas employed was dry carbon monoxide.

Zinc in Carbon Monoxide. Pressure 50 mm.

Temperature.....	560°	600°	620°	640°	660°	680°
Volatilisation, per cent.	7·42	21·62	44·28	58·18	80·66	99·62

Fourth Series.

The foregoing experiments having clearly indicated the nature of the action of pressure in relation to the rate of volatilisation of zinc, it was thought well to conduct a similar series of observations with another metal. For this purpose cadmium was selected. The material used was purchased as chemically pure, but was not analysed. The values obtained were as follow:

I.—*Cadmium in Air. Pressure 10 mm.*

Temperature	330°	370°	405°	420°	450°
Volatilisation, per cent.	0.72	13.08	40.18	49.48	83.68

II.—*Cadmium in Air. Pressure 50 mm.*

Temperature	450°	480°	500°	520°
Volatilisation, per cent.	22.82	46.72	66.14	95.75

III.—*Cadmium in Air. Pressure 100 mm.*

Temperature	500°	520°	540°	560°
Volatilisation, per cent.	24.56	43.14	62.26	78.16

IV.—*Cadmium in Air. Pressure 400 mm.*

Temperature	580°	600°	640°
Volatilisation, per cent.	36.24	57.32	93.12

V.—*Cadmium in Air. Pressure 600 mm.*

Temperature	620°	660°	680°
Volatilisation, per cent.	36.12	72.54	89.79

Consideration of the Results.

A brief examination of the above figures will prove that the rate of volatilisation of both zinc and cadmium at a given temperature is much diminished by even very small gaseous pressures; it is also evident that both hydrogen and carbon monoxide, at low pressures, produce nearly as marked an effect as air; although hydrogen has distinctly less effect than air as the pressures increase. More detailed conclusions can, however, be drawn from the plotting of rate-temperature curves as given in Figs. 2 and 3.

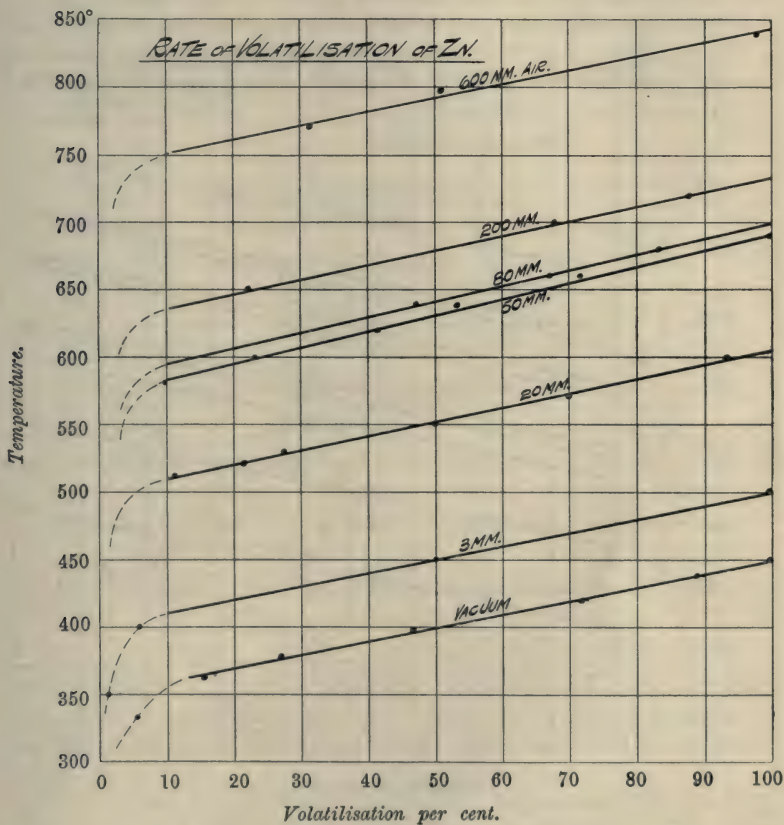
The values observed when zinc is heated in air are represented in Fig. 2. It will be readily observed that, when once a rate of loss equal to about 10 per cent. in thirty minutes has been reached, the experimental points lie, within the limits of error, on straight lines. Further, all the straight lines are sensibly parallel, showing that when a certain critical temperature, depending on the pressure, has been reached, the increase of volatilisation is directly proportional to the rise of temperature, and independent of the original pressure. In every case when starting with the temperature necessary to produce 10 per cent. volatilisation, it is found that by raising the temperature about 90°, the rate of volatilisation is increased to 100 per cent., the time interval remaining constant.

It may be here noted that Greenwood (*Chem. News*, 1911, **104**, 43) has observed, in reference to the boiling points of metals, that

"the difference between the temperature indicated when a gentle agitation is first apparent and that at which ebullition has become violent . . . does not exceed 100° ."

It will further be noted that whilst the first increase of pressure of only 3 mm. raised the critical point by about 50° , the later increase of 400 mm. (from 200 to 600 mm.) only raised the critical temperature by about 120° . In the first case, 1 mm. raised the

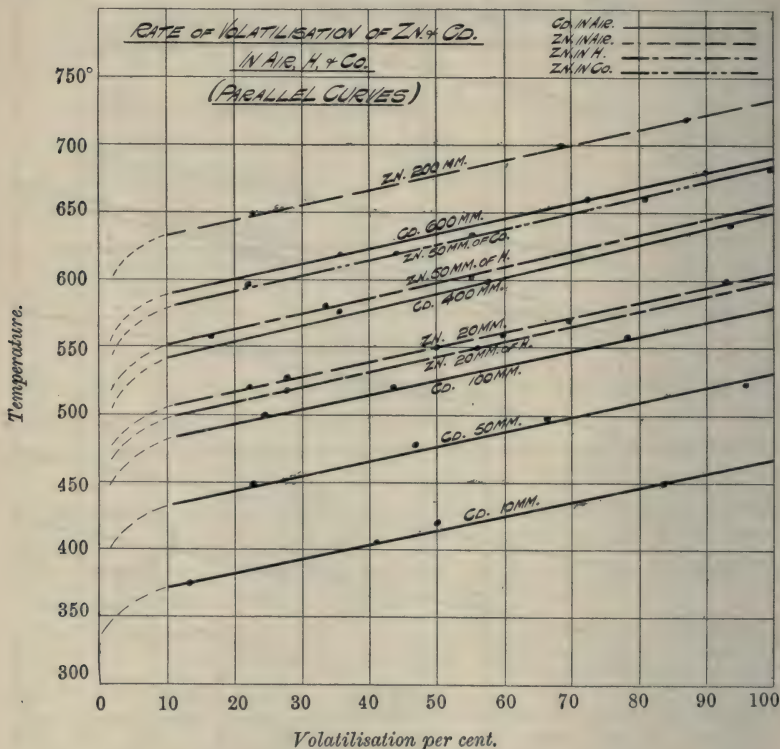
FIG. 2.



temperature by about 20° , and in the second, by only 0.3° ; the marked effect of even a minute leak is thus fully obvious. From a practical point of view it may be expressed in this way: that the removal of the last mm. of gaseous pressure produces about seventy times the effect in lowering the temperature of effective distillation as compared with the removal of 1 mm. when starting with any pressure in excess of 50 mm.

Turning now to Fig. 3, which contains the results of heating cadmium in air under various pressures, and also of zinc in hydrogen and in carbon monoxide, it will be noted that all the curves are again straight lines after the critical temperature has once been reached. These lines are not only all parallel to each other, but also parallel to the 20 mm. and the 200 mm. zinc in air lines which are reproduced for purposes of comparison. They are therefore also parallel to the line for zinc in a vacuum, which is

FIG. 3.



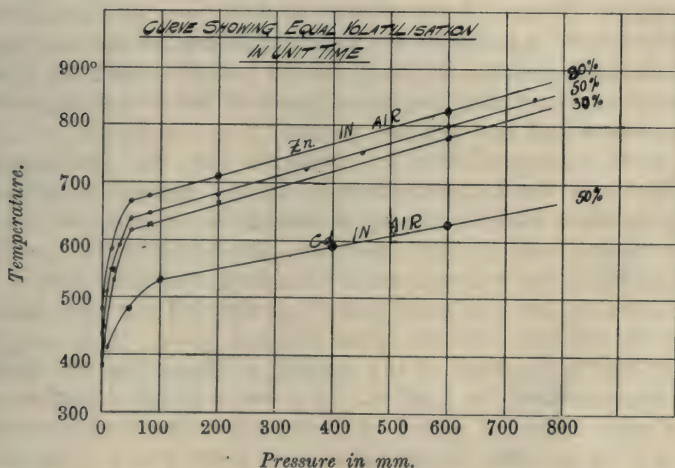
the base line in Fig. 2. There are therefore two metals, three gaseous atmospheres, and 16 series of pressure observations, all of which yield parallel straight lines when once the critical rate of volatilisation has been reached.

It might perhaps have been anticipated that as the mass of metal remaining in the boat was steadily decreasing during the course of an experiment, the rate of loss would diminish as the weight of metal became less. The law of Ramsay and Young,

however, states that the rate of evaporation at the surface of a solid is independent of the extent of the surface, but is influenced only by the rate at which heat is communicated to it. The law may apparently be extended to the case of the distillation of metals, and we conclude that when that temperature has been reached at which vaporisation proceeds freely, any increase in the rate of distillation is independent of the pressure, or the nature of the gas, and that it varies directly with the temperature.

If it is desired to maintain an equal rate of volatilisation, while the pressure and temperature are varied, the relationship is not so simple, as will be seen in reference to Fig. 4, in which are a few typical curves showing equal rates of volatilisation plotted

FIG. 4.



against temperature and pressures. The unit of time, in each case, is, as before, thirty minutes. The gas employed is air, and the metal is zinc in the upper curves, and cadmium in the lower curve.

These curves were obtained partly from intersections in the lines given in Figs. 2 and 3, and partly from direct experiments. The figures used in plotting the 50 per cent. zinc volatilisation curve are as follow:

Pressure	vacuum	3 mm.	10 mm.*	20 mm.	30 mm.*	40 mm.*
Temperature	400°	450°	510°	550°	590°	620°
Δ		21	8.5	4	4	3

Pressure	50 mm.	80 mm.	200 mm.	350 mm.*	450 mm.*	600 mm.	750 mm.*
Temperature ...	640°	645°	680°	725°	755°	800°	850°
Δ	2	0.16	0.3	0.3	0.3	0.3	0.3

Those marked with an asterisk are from direct experiments. The sign Δ is used to indicate the mean rise in temperature necessary to compensate for the effect of an increase of pressure of 1 mm. The values for 30 and 80 per cent. volatilisation of zinc are obtained from the curves in Figs. 2 and 3. The values for cadmium were also deduced from Fig. 3, and the numbers are as follow:

Pressure	10 mm.	50 mm.	100 mm.	400 mm.	600 mm.
Temperature	415°	480°	530°	590°	630°
Δ	1.5	0.5	0.2	0.2	

It will be observed that in the case of zinc there is an abrupt change of direction at about 50 mm. pressure. Up to that point the curve is steep, and the effect of small additions of pressure is very marked, although steadily decreasing. Beyond the bend, from a pressure of 80 mm., the curves are straight lines, and the increase of temperature is proportional to the pressure. A similar change of direction is observed in the curve for cadmium, and the change occurs at approximately the same pressure, but the straight lines for cadmium and zinc are not parallel.

A point worthy of note in connexion with the distillation of zinc in air is the marked difference in the amount of oxidation according as to whether the air is moving or at rest. So long as there was no leak in the apparatus, the oxidation of the zinc, even at 800°, was so small as to be almost negligible. In a few cases there was an accidental leak of air through the joint between the porcelain tube and the glass covering plate. This leak was usually due to the heat of the furnace softening the sealing-wax, and was recognised by a fall in the pressure gauge. Such experiments were discarded so far as numerical values were concerned, but in all such cases it was noted that there was a considerable quantity of zinc oxide produced. A small quantity of air in motion appears to produce more oxidation than a considerably larger quantity at rest in the porcelain tube. In still air the heavy zinc vapour probably rises gradually, and displaces the air without combining with the oxygen just as air may be displaced from a vessel by a liquid or a heavier gas.

Conclusions.

1. It is necessary to heat a metal to some definite temperature in order to obtain a rate of volatilisation which is readily appreciable.

2. This necessary temperature or critical point is raised by gaseous pressure, the first small additions having the most marked effect.

3. When this critical point has once been reached for the particular metal and pressure employed, the rate of volatilisation is independent of the initial pressure, or the nature of the gas (so long, of course, as this does not attack the metal), but it increases directly with the rise of temperature. All rate-temperature curves are therefore parallel straight lines throughout the greater part of their length. Hence if R be the percentage rate of volatilisation at a certain temperature, at or above the critical point, and R' at some higher temperature, then

$$R' = R + at,$$

the value of a in this case being approximately equal to unity.

4. The initial temperature is raised rather less by carbon monoxide than by air, and still less by hydrogen. The differences are, however, at low pressures, too small to be of practical importance.

5. The pressure-temperature curve for equal rates of volatilisation is steep from 0 to 50 mm. There is an abrupt change of direction at 50 mm., and from 80 mm. onwards it becomes a straight line much less steeply inclined. The curves for zinc and cadmium are not parallel.

6. On exhausting down to about 50 mm., each mm. removed leads to a small but equal effect in lowering the volatilisation temperature. This effect is, however, only about one-seventieth of that due to the removal of 1 mm. when a perfect vacuum is nearly reached.

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CLXV.—Contributions to the Chemistry of the Terpenes. Part XVI. The Oxidation of Bornylene with Hydrogen Peroxide.

By GEORGE GERALD HENDERSON and WILLIAM CAW.

IN continuation of our study of the action of hydrogen peroxide on the terpenes (compare T., 1911, **99**, 1539; 1912, **101**, 2288), we have examined the behaviour of bornylene towards that oxidising agent. When dissolved in glacial acetic acid, the hydrocarbon is slowly oxidised by 30 per cent. aqueous hydrogen peroxide, being converted into a mixture of free acids and of esters; a trace of an aldehyde was detected among the products of oxidation, but no ketone was formed under the conditions of our experiments.

Two of the three acids produced by the oxidation of bornylene are crystalline solids, which volatilise in a current of steam. They were separated by fractional crystallisation from glacial acetic acid and identified as camphenanic acid, $C_9H_{15} \cdot CO_2H$, m. p. 95° , and the isomeric *isocamphenanic* acid, m. p. 74° , respectively. The third acid, which was present in comparatively small quantity, does not volatilise in steam, and could not be obtained in the crystalline state; it is a colourless, viscous liquid, which undergoes decomposition when distilled, even under diminished pressure. Analyses of its *methyl* ester and of its *silver* salt lead to the conclusion that it is a *hydroxy-acid* of the formula $C_8H_{12}(OH) \cdot CO_2H$. When distilled under diminished pressure, it yields a crystalline, unsaturated *acid*, m. p. about 80° , which for the present has not been further examined.

The neutral oxidation product was found to consist of a mixture of esters, and was separated by steam distillation into a volatile and a non-volatile portion. The volatile portion yields on hydrolysis (1) acetic acid, with much smaller quantities of camphenanic and *isocamphenanic* acids and the liquid acid, and (2) a mixture of two isomeric alcohols of the formula $C_{10}H_{17} \cdot OH$, which were separated by fractional crystallisation from light petroleum. As might have been anticipated, the alcohol present in largest quantity was found to be borneol. The other alcohol is a crystalline solid, which melts at 180° . On oxidation with chromic acid mixture it is converted into a ketone, which resembles camphor in appearance, melts at 184° , and yields an oxime melting at 103° . The second alcohol is thus proved to be epiborneol.

The portion of the mixture of esters which did not volatilise in steam gave, when hydrolysed, (1) acetic acid with much smaller quantities of the other acids, and (2) a mixture of two isomeric *alcohols* of the formula $C_{10}H_{18}O_2$. These alcohols, which were separated by fractional crystallisation from benzene, are crystalline solids melting at $247-248^\circ$ and $235-236^\circ$ respectively. They are saturated, and do not react with semicarbazide acetate; they are readily oxidised by chromic mixture, and when heated with water containing a little sulphuric acid are converted into compounds which volatilise easily in a current of steam; they react with phthalic anhydride to form acid phthalates, and with phenylcarbimide, but in each case the products could not be induced to crystallise; on treatment with *p*-nitrobenzoyl chloride they yield crystalline *p*-nitrobenzoates. Lack of material has prevented us from ascertaining whether or not these alcohols are dihydric; we propose to prepare and examine larger quantities in order to settle this point.

The most interesting result of this investigation is the direct

formation of camphenanic and *isocamphenanic* acids from pure bornylene, because these acids have already been prepared from camphene by two different methods; first, by oxidising camphene with hydrogen peroxide (Henderson and Sutherland, T., 1911, **99**, 1539), and secondly, by Aschan, as the result of the action of potassium permanganate in acetic acid on camphene at a low temperature. The constitution of camphenanic and *isocamphenanic* acids has not yet been determined, although we hope that experiments at present in progress will throw light on this question, but their formation from bornylene as well as from camphene undoubtedly lends support to the view already expressed by one of us (compare T., 1911, **99**, 1901) that there must be much closer similarity in the constitution of these terpenes than is indicated by the formulæ usually assigned to them.

EXPERIMENTAL.

Oxidation of Bornylene.—A number of preliminary experiments, in which the effects of varying the temperature and the proportions of the solvent and of the oxidising agent were studied, led to the adoption of the following process. A solution of 50 grams of bornylene* (1 mol.) in 350 c.c. of glacial acetic acid was placed in a flask provided with an air condenser, 120 c.c. of a 30 per cent. aqueous solution of hydrogen peroxide (3 mols.) were added, and the mixture was heated at a temperature of 55–60°. At the beginning of the operation fairly large quantities of bornylene volatilised into the neck of the flask, and in order to avoid loss of the extremely volatile hydrocarbon the mixture was cooled at intervals and the crystalline deposit returned to the mother liquor. As the heating was continued the volatilisation of the bornylene gradually diminished, and after a considerable period, usually about twelve days, entirely ceased; at this stage the oxidation was practically complete. The solution was then diluted with about a litre of water, sodium carbonate was added in small quantities at a time until the acetic acid was almost completely neutralised, and the mixture of oxidation products, which had separated as a viscid, yellow oil, was removed by agitation with ether. Under these conditions only very small quantities of the acids which had been formed from the bornylene were dissolved by the sodium carbonate.

If less than three molecular proportions of hydrogen peroxide are used some of the bornylene escapes oxidation; a larger proportion leads to an increase in the quantity of the acid oxidation products and a diminution in the quantity of neutral products. If the

* The bornylene was purified by the method described in a former paper (Henderson and Caw, T., 1912, **101**, 1416).

temperature is raised much above 60° decomposition of the hydrogen peroxide with consequent loss of oxygen set in. In one experiment acetone was substituted for acetic acid as the solvent, but the result was not satisfactory, for even after prolonged heating very little of the bornylene was oxidised.

Separation of the Acid Oxidation Products.—The ethereal solution of the oxidation products was washed with water and dried with anhydrous sodium sulphate, and after removal of the ether the oily residue was warmed with successive quantities of aqueous sodium carbonate until nothing more passed into solution. The mixed alkaline solutions were cooled, agitated several times with ether in order to remove the undissolved neutral products of oxidation, and then acidified with dilute sulphuric acid. The mixture of acids thus liberated was extracted by means of ether, the ethereal solution washed with water and dried with anhydrous calcium chloride, the ether removed by distillation, and the oily residue distilled in a current of steam. The greater part passed over with the steam, and collected in the receiver in the form of a crystalline solid, whilst a much smaller quantity of a very viscous, brown liquid remained in the distilling flask. The crystals were collected, and a small additional quantity of the same substance was obtained by saturating the aqueous distillate with ammonium sulphate and agitating it with ether.

The crystalline product was found to be a mixture of two acids, which were separated from one another by repeated fractional crystallisation from glacial acetic acid. To a solution of the acids in the least possible quantity of cold acetic acid water was added until a faint turbidity appeared, and the flask was then placed in the ice-chest. After some hours the crystals which had deposited were collected, and the mother liquor was treated similarly with more water and again cooled. Four or five crops of crystals were thus obtained, and after each had been subjected to the same treatment several times a practically complete separation was effected. The less soluble acid melted at 95°, and on analysis was found to have the formula $C_{10}H_{16}O_2$. In all its properties it showed the closest possible resemblance to camphenanic acid, and a mixture of the two melted sharply at 95°; there can be no doubt as to their identity. The more soluble acid has the same formula, but its melting point is 74°; it was proved to be isocamphenanic acid.

The acid which did not pass over with steam was separated from the water in the distillation flask by means of ether. After drying the ethereal solution with anhydrous calcium chloride, the acid was obtained on removal of the ether as a very viscid liquid of a brownish-yellow colour. It is very readily soluble in all the usual

organic solvents with the exception of light petroleum, in which it is practically insoluble, and it dissolves rather sparingly in hot water; from none of these solvents could it be induced to separate in crystalline form. Distillation as a means of purification was not available, for even under diminished pressure the acid undergoes partial decomposition. It was finally purified by conversion into, and subsequent hydrolysis of, its methyl ester, and was thus obtained as a colourless, viscid liquid.

Attempts to prepare crystalline sodium and calcium salts of the liquid acid were unsuccessful, because these salts are extremely readily soluble in water, and on concentration of the solutions form jellies, which on further heating dry up to horny masses. When dry ammonia is passed into a solution of the acid in dry ether a solid ammonium salt is formed, which, however, changes at once to a sticky mass when the ether is removed. The *silver* salt, $C_9H_{13}O_3Ag$, separates as a white, crystalline solid on addition of silver nitrate to a concentrated solution of the sodium salt; it is readily soluble in water, and is easily decomposed by heat or by exposure to light. (Found, $Ag = 38.3$. Calc., $Ag = 39$ per cent.)

The *methyl ester* of the liquid acid was prepared by treatment of a concentrated aqueous solution of the sodium salt with excess of methyl sulphate, and purified by distillation under diminished pressure. It is a colourless liquid with a pleasant odour, which boils at $160-162^\circ/24$ mm.:

0.2131 gave 0.5088 CO_2 and 0.1754 H_2O . $C = 65.1$; $H = 9.1$.

$C_{10}H_{16}O_3$ requires $C = 65.2$; $H = 8.7$ per cent.

When the liquid acid is distilled under diminished pressure partial decomposition ensues, and a different acid is obtained. The new *acid* volatilises readily in a current of steam, and crystallises from dilute methyl alcohol in colourless needles, which melt at about 80° . It is almost insoluble in water, but dissolves freely in the usual organic solvents, and towards permanganate behaves as an unsaturated compound. The calcium salt of this acid is crystalline and sparingly soluble in water.

Taking all these facts into consideration it is probable that the liquid acid is a *hydroxy-acid* of the formula $C_8H_{12}(OH) \cdot CO_2H$.

Separation and Examination of the Neutral Oxidation Products.—The ethereal solution of the neutral oxidation products, from which the free acids had been removed by treatment with aqueous sodium carbonate, was washed with water and dried with anhydrous sodium sulphate. On removal of the ether an oily liquid with a strong odour was obtained. Small portions of this liquid were tested for ketones with semicarbazide hydrochloride, for alcohols with phenylcarbimide, and for aldehydes with a saturated solution

of sodium hydrogen sulphite. The two former reagents gave negative results; with the last, traces of a crystalline bisulphite compound were formed, but the quantity was so small as to be negligible. The bulk of the neutral product was now heated in a current of steam, with the result that a portion passed over with the steam and a portion remained in the distilling flask.

The volatile part was separated from the aqueous distillate by means of ether. The ethereal extract was dried, and on removal of the ether by distillation an oily liquid with an odour somewhat like that of borneol was left in the flask. A small portion of this liquid was distilled under diminished pressure, and yielded a large fraction, which boiled at about $104^{\circ}/20$ mm., and smaller fractions of higher boiling points. The fraction of lowest boiling point was found to be composed of esters of acetic acid, the next higher of esters of camphenanic and *isocamphenanic* acid, and the highest of esters of the liquid acid, but the separation of these was far from complete. Consequently the bulk of the liquid was hydrolysed by heating for some hours under a reflux condenser with methyl-alcoholic potassium hydroxide. After cooling, the solution was mixed with water and agitated several times with ether. The ethereal solution was washed with water and dried with anhydrous sodium sulphate, and the ether removed by evaporation under diminished pressure. The crystalline solid which remained was readily soluble in alcohol, ether, and other solvents, but by fractional crystallisation from light petroleum was ultimately found to be a mixture of two alcohols. The less soluble alcohol, which was present in considerably the greater proportion, melted after purification at 208° , and was proved to be borneol. The more soluble alcohol melted at $170-175^{\circ}$, and for purification was converted into the acid phthalate by the usual method. After several crystallisations from light petroleum this ester was obtained in colourless crystals, which melted sharply at 166° . On hydrolysis of the acid phthalate a saturated alcohol was obtained, which crystallised from dilute methyl alcohol in long, colourless needles, melting at 172° ; on recrystallisation from light petroleum the melting point rose to 180° . On oxidation with chromic acid mixture the alcohol is converted into a ketone, which crystallises in waxy leaflets, melts at 183° , volatilises very readily in a current of steam, and yields an oxime melting at 103° . Hence it is evident that the second alcohol is epiborneol.

The acids liberated by hydrolysis of the mixture of volatile esters were mainly acetic acid, with much smaller quantities of camphenanic, *isocamphenanic*, and the liquid acids.

The portion of the neutral oxidation products which did not

volatilise in a current of steam was likewise found to consist of a mixture of esters which could not be satisfactorily separated by distillation under diminished pressure, and therefore was hydrolysed by heating for several hours under a reflux condenser with methyl-alcoholic potassium hydroxide. When the hydrolysis was completed, the methyl alcohol was removed by distillation, and the residual mixture agitated several times with ether. The ethereal solution was washed with water and dried with anhydrous sodium sulphate, and on removal of the ether a crystalline residue was obtained, which was found to be a mixture of two alcohols. These were separated from each other by fractional crystallisation from benzene.

The less soluble alcohol, after purification by several crystallisations from benzene, was obtained in colourless, lustrous leaflets, which melt at 247—248° in a closed tube. It is somewhat sparingly soluble in cold benzene, readily so in alcohol or ether, almost insoluble in light petroleum, and soluble to some extent in water:

0.2053 gave 0.5288 CO₂ and 0.2019 H₂O. C=70.3; H=10.9.

0.2252 „ 0.5803 CO₂ „ 0.2175 H₂O. C=70.2; H=10.7.

C₁₀H₁₈O₂ requires C=70.6; H=10.6 per cent.

The phenylurethane and the acid phthalate of this alcohol were prepared by the usual methods, but only in the form of viscous substances. A crystalline *p*-nitrobenzoate was obtained by heating the alcohol, dissolved in pyridine, for several hours with a slight excess of *p*-nitrobenzoyl chloride. After cooling, the pyridine was dissolved by addition of dilute sulphuric acid, and the crude ester which remained was shaken with dilute aqueous sodium carbonate, dried, and crystallised from light petroleum. From this solvent the *p*-nitrobenzoate separates in pale yellow, silky needles, which melt at 44—45°. It is readily soluble in alcohol or ether. The quantity obtained was too small to permit of satisfactory analysis.

The alcohol does not react with semicarbazide hydrochloride. When heated with water containing a little sulphuric acid it is quickly converted into a compound, which volatilises readily in a current of steam. This compound crystallises from dilute methyl alcohol in small, colourless prisms, with a strong odour, which melt at 169°. On oxidation with chromic mixture the alcohol yields a compound which also volatilises in steam, and which crystallises from light petroleum in colourless plates, melting at 165—166°. Further examination of these compounds is necessary, but it seems probable that the alcohol is either a glycol or an oxide alcohol.

The more soluble alcohol of the formula C₁₀H₁₈O₂ was obtained on concentration of the benzene solution from which the less soluble isomeride had separated, and purified by several crystallisations

from benzene. It separates from that solvent in radiating clusters of fine needles, which melt at $235-236^{\circ}$ in a closed tube. It is readily soluble in alcohol, ether, or benzene, sparingly so in light petroleum:

0.2039 gave 0.5268 CO_2 and 0.1990 H_2O . $\text{C}=70.2$; $\text{H}=10.8$.

0.2194 „ 0.5648 CO_2 „ 0.2120 H_2O . $\text{C}=70.3$; $\text{H}=10.7$.

$\text{C}_{10}\text{H}_{18}\text{O}_2$ requires $\text{C}=70.6$; $\text{H}=10.6$ per cent.

The acid phthalate and the phenylurethane of this alcohol were also obtained as viscous substances, and its behaviour towards semicarbazide hydrochloride, dilute sulphuric acid, and chromic mixture respectively was exactly similar to that of the less soluble isomeride. A small quantity of a *p*-nitrobenzoate was obtained in minute, pale yellow needles, which melted at $82-83^{\circ}$.

The acids obtained on hydrolysis of the mixture of esters of these two alcohols were chiefly acetic acid, and, in much smaller quantity, camphenanic acid, *isocamphenanic acid*, and the liquid acid.

We take this opportunity of expressing our thanks to the Carnegie Trust for a grant which defrayed most of the expense of this work.

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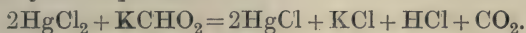
CLXVI.—*The Reduction of Mercuric Chloride by Sodium Formate.**

By ALEXANDER FINDLAY and MORTON JAMES PRYCE DAVIES.

THE reduction of mercuric chloride was proposed by Portes and Ruyssen (*Compt. rend.*, 1876, **82**, 1504) as a method for the quantitative determination of formic acid and formates; and it was pointed out at a later time by Scala (*Gazzetta*, 1890, **20**, 393) that the method could be employed for the quantitative determination of formic acid in the presence of acetic and butyric acids. It was, however, shown by Lieben (*Monatsh.*, 1893, **14**, 750) that Scala's method is accurate only when five to six times the theoretical quantity of mercuric chloride is employed and when the mixture is

* The present (preliminary) communication is an abstract of part of a thesis submitted by one of the authors for the degree of M.Sc. of the University of Wales. This abstract is published at the present time on account of a communication having recently been made by G. A. Linhart (*Zeitsch. anorg. Chem.*, 1913, **82**, 1) on the reduction of mercuric chloride by phosphorous acid.

heated for six to eight hours on a water-bath. The reaction he represented by the equation:



The present investigation was undertaken with the object of studying this reduction process more fully, and a number of experiments were carried out for the purpose of obtaining information with regard to the kinetics of the reaction. This seemed to be of all the greater interest by reason of the fact that the process of reduction of mercuric chloride by phosphorous acid had been the subject of investigation by Montemartini and Egidi (*Gazzetta*, 1902, **32**, ii, 182), who, however, arrived at no definite conclusion with regard to the order of the reaction. An investigation by Garner, Foglesong and Wilson (*Amer. Chem. J.*, 1911, **46**, 361), published after an investigation had been commenced, was equally unsatisfactory; but, recently, Linhart (*Zeitsch. anorg. Chem.*, 1913, **82**, 1) has shown that the reaction is a bimolecular one.

The reduction of silver acetate by sodium formate was studied by Noyes and Cottle (*Zeitsch. physikal. Chem.*, 1898, **27**, 579), who concluded that the reaction was of the third order.

Although we have carried out experiments at 40°, 50°, 60°, 70°, and 85.5°, we shall, in the present communication, give the results only of the experiments at 40°.

EXPERIMENTAL.

The method employed was to mix 100 c.c. of a solution of sodium formate (the concentration of which was determined by means of permanganate) with 100 c.c. of a solution of mercuric chloride, both at the temperature of the thermostat (40°). After given intervals of time, 10 c.c. of the mixture were removed by means of a pipette fitted with a small filtering plug, and run into excess of a standard solution of potassium iodide. The excess of iodide was then titrated by means of a standard mercuric chloride solution.

On calculating the values of the velocity-coefficient according to the equation for a reaction of the second order, it was found that the values gradually diminished. As it had been found that the reduction of mercuric chloride by formic acid took place more slowly than with sodium formate, the falling off in the values of the velocity-coefficient was attributed to the formation of hydrochloric acid (hydrion) during the reaction. A quantity of sodium acetate was therefore added to the mixture, and this was found to render the values of the velocity-coefficient more constant.

In table I are given the detailed results obtained in one experiment and in table II are summarised the results of other experiments carried out with different initial concentrations of the react-

ing substances. In each case a represents the initial concentration of mercuric chloride in mols. per litre, and b the concentration of sodium formate. The values under K_2 are calculated by means of the equation:

$$K_2 = \frac{2.30}{t(a-b)} \cdot \log_{10} \frac{b(a-x)}{a(b-x)},$$

and those under K_3 by the equation:

$$K_3 = \frac{1}{t} \cdot \frac{1}{(b-a)^2} \left\{ \frac{(b-a)x}{a(a-x)} + 2.30 \log_{10} \frac{b(a-x)}{a(b-x)} \right\}.$$

The time is expressed in hours.

TABLE I.

$$a = 0.1040; b = 0.3685.$$

t .	$a-x$.	x .	$b-x$.	K_2 .	K_3 .
0.3	0.0932	0.0108	0.3557	1.018	10.24
0.6	0.0831	0.0209	0.3476	1.044	11.29
0.9	0.0756	0.0284	0.3401	1.000	11.41
1.2	0.0693	0.0347	0.3338	0.966	11.53
1.6	0.0613	0.0427	0.3258	0.957	12.29
2.0	0.0553	0.0487	0.3198	0.913	12.52
2.3	0.0509	0.0531	0.3154	0.922	13.04
2.7	0.0461	0.0579	0.3106	0.904	13.51
3.0	0.0429	0.0611	0.3074	0.887	13.91
5.1	0.0260	0.0780	0.2905	0.852	18.17
Mean.....				0.95	12.7

TABLE II.

		Mean.	
Initial concentrations.	Extreme values.	K_2 .	K_3 .
1. $a = 0.1040; b = 0.3685 \dots$	K_2 : 1.018—0.852 K_3 : 18.17—10.24	0.95	— 12.7
2. $a = 0.1040; b = 0.1889 \dots$	K_2 : 0.861—0.791 K_3 : 9.10—11.50	0.83	— 10.4
3. $a = 0.1040; b = 0.5637 \dots$	K_2 : 1.18—0.93 K_3 : 10.41—16.70	1.02	— 13.4
4. $a = 0.1028; b = 0.3790 \dots$	K_2 : 1.05—0.875 K_3 : 10.79—13.50	0.96	— 12.2
5. $a = 0.1028; b = 0.7802 \dots$	K_2 : 1.07—8.15 K_3 : 10.00—16.04	0.92	— 13.3
6. $a = 0.1028; b = 1.0227 \dots$	K_2 : 1.18—1.01 K_3 : 13.03—16.90	1.11	— 15.2
7. $a = 0.1034; b = 0.1737 \dots$	K_2 : 0.991—0.834 K_3 : 10.12—14.40	0.90	— 12.2
8. $a = 0.1034; b = 0.1737 \dots$	K_2 : 1.011—0.851 K_3 : 9.73—14.83	0.88	— 11.9
9. $a = 0.0503; b = 0.1737 \dots$	K_2 : 0.913—0.839 K_3 : 17.40—27.58	0.87	— 23.8
10. $a = 0.1382; b = 0.1737 \dots$	K_2 : 1.01—0.862 K_3 : 7.86—9.91	0.91	— 9.0
11. $a = 0.1366; b = 0.1739 \dots$ (2.9 grams of sodium acetate in 200 c.c. of mixture)	K_2 : 1.07—0.968 K_3 : 8.21—11.49	0.99	— 10.1

TABLE II.—*continued.*

		Mean.	
Initial concentrations.		K_2	K_3
12.	$a=0.1366$; $b=0.1189...$ (3.5 grams of sodium acetate in 200 c.c. of mixture)	K_2 : 1.09 — 1.00 K_3 : 8.49 — 9.71	1.04 — 9.2
13.	$a=0.0925$; $b=0.1454...$ (3.6 grams of sodium acetate in 200 c.c. of mixture)	K_2 : 1.09 — 0.991 K_3 : 12.74 — 16.97	1.02 — 14.3
14.	$a=0.0688$; $b=0.2942...$ (1.8 grams of sodium acetate in 200 c.c. of mixture)	K_2 : 1.07 — 0.969 K_3 : 18.4 — 27.21	1.02 — 22.1

Even although in any given case the values of the velocity-coefficient vary during the course of the reaction, whether the coefficient be calculated according to the equation for a reaction of the second or of the third order, the mean values obtained with different initial concentrations are quite obviously more constant in the former case; and more especially is this true when sodium acetate is added to the reaction mixture. From these values, then, the conclusion may be drawn that the reduction of mercuric chloride by sodium formate is a bimolecular reaction.

This conclusion is also borne out by the application of the van't Hoff differential method of determining the order of a reaction, as is shown by the numbers in table III.

TABLE III.

I. $b=0.1737$.

t .	a_1 .	da_1/dt .	t .	a_2 .	da_2/dt .	n .
0	0.1034	0.0118	0	0.0503	0.0059	0.96
3	0.0679		3	0.0326		
0	0.1382	0.0134	0	1.0227	0.0648	0.76
4	0.0845		4	0.9579		

II. $a=0.1028$.

0	0.3790	0.02323	0	1.0227	0.0648	0.99
2.2	0.3279		1	0.9579		
0	0.3790	0.02323	0	0.7802	0.0522	1.07
2.2	0.3279		1	0.7280		

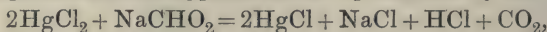
These numbers show, then, that the reaction is unimolecular with reference both to mercuric chloride and to sodium formate.

That the reaction is unimolecular with reference to mercuric chloride was also found by the method of integration for the same fractional parts of the reacting substance.

For constant concentration of sodium formate ($b=0.1737$) and varying concentrations of mercuric chloride ($a_1=0.1603$, $a_2=0.1034$; $a_3=0.0503$) the following values of the time required for a given fraction of the reaction to take place were found:

$$\begin{array}{ll} \text{For } (a-x) = \frac{1}{3} \begin{cases} t_1 = 3.35 \\ t_2 = 2.85 \\ t_3 = 2.80 \end{cases} & \begin{array}{l} t_1 : t_2 = 1.17 \\ t_1 : t_3 = 1.19 \\ t_2 : t_3 = 1.02 \end{array} \\ \text{For } (a-x) = \frac{1}{2} \begin{cases} t_1 = 6.5 \\ t_2 = 5.4 \\ t_3 = 5.0 \end{cases} & \begin{array}{l} t_1 : t_2 = 1.2 \\ t_1 : t_3 = 1.3 \\ t_2 : t_3 = 1.08 \end{array} \end{array}$$

It appears then, to be established that the reduction of mercuric chloride by sodium formate is a reaction of the second order, and as the complete reaction appears to be represented by the equation:



it follows that the reaction must take place in stages.

A similar conclusion has just been arrived at by Linhart (*loc. cit.*) for the reduction of mercuric chloride by phosphorous acid, the order of the reaction in this case being explained on the assumption that the slow reaction which is measured is the oxidation of the phosphorous acid to hypophosphoric acid. That a similar explanation can be offered in the case of the reduction of mercuric chloride by sodium formate appears to be very doubtful; but as the investigation is still in progress we shall defer the discussion of the mechanism of the reaction until the experiments which are at present in progress have been completed.

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CLXVII.—*Polybromides in Nitrobenzene Solution.*

By ALFRED FRANCIS JOSEPH.

In a recent communication (T., 1911, **99**, 274) it was shown that the colour of bromine solutions in aqueous potassium bromide led to the same results for the constitution of the polybromide as was obtained by other methods, as, for example, those of Roloff (*Zeitsch. physikal. Chem.*, 1894, **13**, 327) and Worley (T., 1905, **87**, 1107). Attempts have now been made to apply the colorimetric method to the study of nitrobenzene solutions of polybromides; the work was preceded by the determination of the solubility of potassium bromide in nitrobenzene solutions of bromine.

The nitrobenzene was purified by freezing and several subsequent distillations, until the colour, as observed in a colorimeter against weak potassium chromate, remained unchanged after further purifying treatment. It may be noted that the colour of the liquid is lighter when cold than hot, and that it increases perceptibly within a few days of its distillation. The specific resistance of the purified compound was about 1.5 megohms.

Bromine appears to be miscible with nitrobenzene in all proportions. It is usually stated to have no action on cold nitrobenzene, and a qualitative test shows that no appreciable amount of hydrogen bromide is present in a fairly concentrated solution of bromine in nitrobenzene several days old. The conductivity of such a solution, however, shows a marked increase on keeping, indicating the formation of hydrogen bromide. The following example shows the effect of time on the conductivity of a 5 per cent. solution:

Time.	0.	10 min.	1 hour.	18 hours.	28 days.
Conductivity (mhos. $\times 10^{-5}$) ...	1.7	2.9	4.7	7.8	23

According to Dawson (T., 1908, **93**, 2068), the specific conductivity of a polyiodide in decinormal nitrobenzene solution is about 200×10^{-5} ; if that of a polybromide is similar, the above numbers indicate the presence of only a very small proportion of hydrobromic acid, and it has not been taken into account.

The solubility of potassium bromide in nitrobenzene is exceedingly small; accurate determinations have not been made, but it appears to be of the order of 10^{-8} gram-molecules per litre. In the presence of bromine, however, it is considerable, and was determined by shaking the pure dry salt with bromine and nitrobenzene in a thermostat at 28.5° for some hours, and then determining the bromine by means of potassium iodide and standard sodium thiosulphate, and the bromide by titrating with silver nitrate. It was not found necessary to remove the nitrobenzene for the analysis; before titrating with silver nitrate, however, the bromine was removed by the addition of water and aspirating a current of air through the mixture.

The results are shown below, and it will be observed that the proportion of bromine required to keep the bromide in solution regularly increases with the concentration:

Bromine (gram- molecules).	Potassium bromide (gram- molecules).	Ratio.	Bromine (gram- molecules).	Potassium bromide (gram- molecules).	Ratio.
0.0754	0.0404	1.87	0.694	0.257	2.70
0.105	0.0526	2.00	0.862	0.301	2.86
0.317	0.128	2.48	1.192	0.413	2.89
0.466	0.185	2.52	1.535	0.494	3.11
0.536	0.197	2.71			

Following the solubility measurements, determinations were made of the colour of similar solutions. The method used was that previously described; solutions of bromine in nitrobenzene of varying strength were matched against a non-volatile standard (0.1 per cent. methyl-orange), and a calibration curve was con-

structed showing the relation between colour of bromine solution (of constant thickness) and cm. of the standard. The polybromide solution under examination was then matched against the standard, and from the calibration curve the strength of the bromine solution was obtained having the same colour as the polybromide solution.

The solutions were contained in a small glass cell 1 cm. deep; as the colour of many of them was too intense at this thickness, it was reduced by placing in the cell a small, rectangular block of glass 0.5 or 0.8 cm. thick. Separate calibration curves had to be constructed for these.

The colour of the nitrobenzene itself was quite negligible; that of a thickness of 3 cm. was less than could be matched against a methyl-orange standard ten times as weak as that used in the actual experiments.

The results are shown below. As in the case of aqueous solutions, the colour of polybromide is less than that of an equivalent solution of bromine.

An attempt to calculate the colour of a polybromide solution may be made as follows.

In the experiments previously described, the colour of aqueous potassium polybromide was found to be a constant fraction of that of bromine of the same concentration:

Colour	0.018	0.027	0.037	0.0585	0.0575	0.069	0.0765
Total bromine.....	0.0547	0.0839	0.1062	0.1811	0.1830	0.2060	0.2362
Ratio	0.33	0.32	0.35	0.32	0.33	0.33	0.32
Mean				0.326.			

Now in a nitrobenzene solution of polybromide, the whole of the bromide may be taken as combined, owing to its very small solubility. Then if A be the concentration of the bromide, B that of the bromine, and n the number of molecules of bromine combined with one molecule of bromide, A/n molecules of bromine are combined, and therefore $B - A/n$ is the concentration of the free bromine. If the relative colours of free bromine and polybromide are the same in aqueous and nitrobenzene solutions, the colour of the polybromide is $0.326A/n$, and therefore the total colour is $0.326A/n + B - A/n = B - 0.674A/n$. If the tribromide is the principal constituent of the solution, $n=1$, and the colour $= B - 0.674A$.

KBr = A .	Bromine = B .	Colour (observed.)	Colour (calc.).
0.023	0.0995	0.083	0.084
0.0328	0.0766	0.048	0.054
0.0328	0.232	0.199	0.210
0.0411	0.0714	0.038	0.043
0.0460	0.116	0.077	0.085
0.0526	0.105	0.063	0.069
0.0915	0.214	0.142	0.152
0.010	0.208	0.200	0.201

My thanks are due to Mr. J. N. Jinendradasa for assistance with the analytical part of the work.

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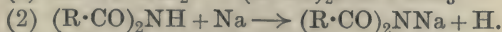
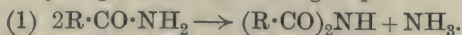
CLXVIII.—*Preparation of Secondary and Tertiary Acid Amides from their Metallic Derivatives.*

By JITENDRA NATH RAKSHIT.

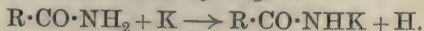
THE replacement of hydrogen in the amido-group of aliphatic amides by alkali metals had been attempted by different investigators through different methods. Curtius (*Ber.*, 1890, **23**, 3037) tried the direct action of metallic sodium on acetamide, and he obtained hydrogen and ammonia as evolved gases, and a yellow, oily liquid, which solidified on cooling. He suspected the substance to be sodium diacetamide, but the investigation was not completed. The formation of sodium diacetamide by the above reaction was indirectly supported by Blacher (*Ber.*, 1895, **28**, 432), who succeeded in isolating diacetamide by the action of an alcoholic solution of sodium ethoxide on the crude product obtained by Curtius's method.

An extensive investigation on the preparation of sodium derivatives of acid amides was undertaken by Titherley (*T.*, 1897, **71**, 466). The principle involved in his process is the interaction of the free acid amides with sodamide in indifferent solvents: $R \cdot CO \cdot NH_2 + NaNH_2 = R \cdot CO \cdot NHNa + NH_2$.

In the present investigation, acid amides were acted on by sodium or potassium in an indifferent solvent, such as benzene or light petroleum. As a rule, sodium causes the condensation of the primary acid amides to secondary ones, and next itself replaces one atom of hydrogen of the amido-group:



It is very curious that the behaviour of potassium under similar conditions is quite different from that of sodium. With formamide it yields potassium diformamide, but with acetamide and propionamide it produces only potassium monacid amides by the simple displacement of one atom of hydrogen:



Sodium Diformamide, $(H \cdot CO)_2NNa$.

Light petroleum was dried by boiling under a reflux condenser with anhydrous potassium carbonate for about three hours, and

the fraction boiling between 65° and 75° was collected and kept in a bottle containing sticks of potassium hydroxide. Two hundred c.c. of light petroleum and 10 grams of formamide are placed in a 750 c.c. flask, then 5 grams of freshly-cut sodium are dropped into the flask, which is immediately attached to a spiral reflux condenser. As soon as sodium dips under the petroleum and reaches the layer of formamide, a brisk evolution of gas commences. The separate pieces of sodium, being covered by layers of amide and bubbles of gas, float again on the surface, during which time a very strong odour of ammonia is perceived at the open end of the condenser. In an hour the reaction practically ceases, when the mass solidifies. It is then heated to boiling over a liquid paraffin bath for four hours to convert any unchanged amide. When cooled, the crystalline, solidified mass is collected with the aid of the pump, and washed three times with light petroleum. It is then kept in a vacuum desiccator over sulphuric acid for twenty-four hours.

0.1243, by Kjeldahl's method, required 13.0 c.c. $N/10\text{-HCl}$.
 $N = 14.72$.

0.6480 gave 0.4840 Na_2SO_4 . $\text{Na} = 24.21$.

$\text{C}_2\text{H}_2\text{O}_2\text{NNa}$ requires $N = 14.73$; $\text{Na} = 24.21$ per cent.

The liberation of hydrogen was estimated quantitatively by the following process. In the above-mentioned flask the sodium is kept in suspension above the liquid by means of a spiral of platinum wire. A tube for the entrance of dry ammonia is introduced into the flask, the end of which just reaches the surface of the light petroleum. The upper end of the condenser is connected to a delivery tube for the collection of gas. The end of the delivery is dipped under a surface of mercury, and the gas is collected by the displacement of dilute sulphuric acid in an inverted cylinder on the trough containing mercury, the mercury preventing the direct contact of gas inside the delivery tube and the dilute acid. The apparatus is freed from air by passing a current of dry ammonia, and, after the air is expelled, the sodium is dropped by vigorous shaking and the reaction at once commences; finally, the flask is heated to boiling. When the reaction is practically finished, a current of ammonia is passed until no more gas is collected over the acid. One gram gave 141 c.c. of moist hydrogen at 33° and 760 mm. pressure, that calculated from the above general equation being 145 c.c. under similar conditions. Hence the reaction is fairly quantitative.

In another experiment the evolved gas was led into dilute hydrochloric acid and converted into the platinichloride (Found, $\text{Pt} = 44.23$; $(\text{NH}_4\text{Cl})_2\text{PtCl}_4$ requires $\text{Pt} = 44.22$ per cent.).

Sodium diformamide is a white, transparent, crystalline compound of pearly lustre. It is extremely deliquescent, readily soluble in water or alcohol, but less soluble in ether or light petroleum.

Potassium Diformamide, $(\text{H}\cdot\text{CO})_2\text{NK}$.

The above experiment was repeated, using, however, 8 grams of potassium instead of the sodium. The reaction with potassium is very vigorous, and a very brisk effervescence takes place. Hydrogen and ammonia gases are evolved. In some cases sparks of light are visible in the earlier stages of the reaction. After the reaction is practically finished, it is boiled for about three hours, when the whole solidifies on cooling. It is collected, washed three times with hot light petroleum, and kept in a vacuum desiccator over sulphuric acid for twenty-four hours:

0.4532 gave 0.3532 K_2SO_4 . $\text{K}=34.96$.

0.3620, by Kjeldahl's method, required 32.6 $\text{N}/10\text{-HCl}$. $\text{N}=12.62$.

$\text{C}_2\text{H}_2\text{O}_2\text{NK}$ requires $\text{K}=35.13$; $\text{N}=12.61$ per cent.

Potassium diformamide is a faintly yellow, crystalline compound; it is extremely deliquescent and readily soluble in water or alcohol, less so in ether or light petroleum.

Sodium Diacetamide, $(\text{CH}_3\cdot\text{CO})_2\text{NNa}$.

Ten grams of acetamide (purified by recrystallisation from benzene), 200 c.c. of anhydrous thiophen-free benzene, and 5 grams of sodium are mixed in a 750 c.c. flask, fitted with a reflux condenser. The reaction does not commence at once. On heating, the acetamide partly dissolves in the benzene, and the rest melts, and the reaction starts at once with the evolution of ammonia and hydrogen. After twenty to thirty minutes, white, flaky crystals begin to separate, and on continuing boiling for three hours the quantity of crystals increases. When cooled, the unconverted acetamide forms a solid crust at the bottom of the flask, and the crystals remain suspended in the benzene, which are then collected and washed three times with hot benzene, and kept in a vacuum desiccator over sulphuric acid (Found, $\text{Na}=18.45$; $\text{N}=11.37$. $\text{C}_4\text{H}_6\text{O}_2\text{NNa}$ requires $\text{Na}=18.69$; $\text{N}=11.38$ per cent.).

Sodium diacetamide forms yellowish-white, shining, flaky crystals. It is deliquescent, readily soluble in water, or alcohol, less so in ether, and practically insoluble in benzene or light petroleum.

Potassium Acetamide, $\text{CH}_3\cdot\text{CO}\cdot\text{NHK}$.

In the preparation of this substance, 10 grams of acetamide, 200 c.c. of benzene, and 4 grams of potassium are boiled as

described above. The reaction commences only on boiling, a faint odour of ammonia is perceived at the beginning, and throughout the reaction hydrogen is evolved. After boiling for an hour, shining, white crystals separate out, and boiling is continued for about four hours. When cold, the crystals are collected, washed with hot benzene, and kept in a vacuum desiccator:

0.3620 gave 0.3254 K_2SO_4 . $K=40.27$.

0.1101 „ 14.3 c.c. N_2 (moist) at 30° and 760 mm. $N=14.48$.

C_2H_4ONK requires $K=40.21$; $N=14.43$ per cent.

Potassium acetamide forms white, flaky, glistening crystals, rapidly deliquescent in air. It is readily soluble in water or alcohol, and sparingly so in ether, benzene, or light petroleum.

Sodium Dipropionamide, $(C_2H_5 \cdot CO)_2NNa$.

Eight grams of propionamide, 150 c.c. of light petroleum, and 3 grams of sodium are boiled together. The reaction then commences, hydrogen and ammonia being evolved. After about an hour, white crystals separate out, the boiling being continued for four hours. When cold, the crystals are collected, washed, and kept in a vacuum desiccator in the usual manner:

0.4530 gave 0.2110 Na_2SO_4 . $Na=15.08$.

0.2446, by Kjeldahl's method, required 16.2 c.c. $N/10-HCl$. $N=9.25$.

$C_6H_{10}O_2NNa$ requires $Na=15.23$; $N=9.27$ per cent.

Sodium dipropionamide forms white, crystalline plates of pearly lustre. It is deliquescent and readily soluble in water or alcohol, but sparingly so in ether, light petroleum, or benzene.

Potassium Propionamide, $C_2H_5 \cdot CO \cdot NHK$.

Eight grams of propionamide, 150 c.c. of dry light petroleum, and 5 grams of potassium are boiled as before. The reaction commences on boiling, and after twenty minutes white crystals are formed. The mixture is boiled for three hours, when fine, white crystals separate. On cooling, these are collected, washed, and kept in a vacuum desiccator:

0.3698 gave 0.2907 K_2SO_4 . $K=35.26$.

0.2680, by Kjeldahl's method, required 24.0 c.c. $N/10-HCl$. $N=12.55$.

C_3H_6ONK requires $K=35.13$; $N=12.61$ per cent.

Potassium propionamide is a white, scaly, crystalline compound, extremely deliquescent, readily soluble in water, or alcohol, but sparingly so in ether, benzene, or light petroleum.

Preparation of Secondary and Tertiary Acid Amides.

Consequent upon the convenient and ready method of preparing sodium derivatives of secondary acid amides, the preparation of diacetamide was undertaken from its derivative. Titherley (T., 1901, **79**, 411) obtained diacetamide by the interaction of acetyl chloride and sodium monoacetamide, and in this connexion he discovered a method of preparing diacetamide by the action of acetyl chloride on acetamide. From sodium diacetamide, however, it can be readily prepared by the action of hydrochloric acid:



Similarly, by the action of acetyl chloride, triacetamide can be obtained:

*Diacetamide, $(\text{CH}_3\cdot\text{CO})_2\text{NH}$.*

Fifteen grams of sodium diacetamide are placed in a 500 c.c. flask, and 62 c.c. of 2*N*-hydrochloric acid in alcoholic solution are added, 5 c.c. at a time; after the addition of each instalment the flask is immediately corked and shaken vigorously by rotatory motion. When all the acid has been added, the flask is connected with a reflux condenser, and heated to boiling for twenty minutes on the water-bath. On cooling, 30 c.c. of dry ether are added, the whole is shaken vigorously and filtered, and the filtrate evaporated on the water-bath. The residue is next extracted, first with 100 c.c., and then with 50 c.c. of warm light petroleum. The petroleum extracts are mixed, filtered, and evaporated on the water-bath. A transparent, shining, crystalline mass is obtained on cooling. The yield is 9.2 grams (Found, *N*=13.59. Calc., *N*=13.86 per cent.).

The diacetamide obtained in this way distilled at 216—218°, and melted at 79°.

Triacetamide, $(\text{CH}_3\cdot\text{CO})_3\text{N}$.

In the preparation of this compound, 10 grams of sodium diacetamide are suspended in 50 c.c. of benzene, and 5.8 c.c. of acetyl chloride are added drop by drop, the mixture being continually shaken; it is finally heated to boiling on the water-bath. The sodium chloride which separates is removed by filtration, and the filtrate evaporated on the water-bath. The residue solidifies on cooling; when crystallised from benzene, it gives transparent, glistening crystals, which melt at 77° (Found, *N*=9.72. Calc., *N*=9.79 per cent.)

I take this opportunity of expressing my best thanks to Prof. P. C. Rây for the interest he has taken in this investigation.

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CLXIX.—*Equivalent Conductivities of Sodium Hyponitrite, Calcium Hyponitrite, and Hyponitrous Acid.*

By PRAFULLA CHANDRA RÂY, RAJENDRALAL DE and NILRATAN DHAR.

THE physical properties of the hyponitrites have not been much studied, probably because of the difficulty of preparing them in a pure state and of their easy decomposibility.

Hantzsch and Kaufmann (*Annalen*, 1896, **292**, 317), from cryoscopic determination of free hyponitrous acid, thought it to be a very feeble acid, but they did not study its electrical properties. We therefore undertook the investigation of the electrical conductivity of the acid and of its sodium and calcium salts.

Sodium hyponitrite was obtained according to the modified method of Divers (T., 1899, **75**, 97), which consists in separating the salt from alkali and traces of hydroxylamine by means of a large excess of absolute alcohol. The only possible impurity which may contaminate the sodium hyponitrite prepared by the above method, is sodium carbonate. With due precaution, however, the sodium salt could be obtained free from this impurity. Calcium hyponitrite was obtained from sodium hyponitrite by double decomposition with calcium chloride. Hyponitrous acid was obtained by the interaction of hydrochloric acid and silver hyponitrite as usual. Divers has not given any specific directions how to prepare the acid. According to him, hyponitrous acid may be obtained by the action of the calculated amount of dilute hydrochloric acid and silver hyponitrite; and this has found expression in many standard textbooks, for example, Roscoe and Schorlemmer's "Treatise on Chemistry," Vol. I, Fourth Edition, 1911. We could not, however, prepare the acid free from hydrochloric acid simply by pouring hydrochloric acid on silver hyponitrite and gently shaking the mixture, even when silver hyponitrite was present in large excess. Apparently the reaction takes place on the surface of the particles of silver hyponitrite, and the insoluble silver chloride forms a protective coating thereon and prevents further action. It could

be obtained absolutely free from hydrochloric acid by gently triturating in a mortar a very large excess of silver hyponitrite with dilute cooled hydrochloric acid. During trituration, precaution was taken to keep the mixture very cold, and the operation was performed as quickly as possible to avoid traces of nitrous acid being formed. The hydrochloric acid used in these preparations was specially prepared by dissolving hydrogen chloride in "conductivity" water. The purity of the hyponitrous acid prepared was tested by adding a portion of the acid to a solution of potassium iodide in dilute sulphuric acid, when a very faint yellow coloration developed in case of stronger acids, and almost no coloration in case of dilute ones. The hyponitrous acid was estimated by titration with a decinormal permanganate solution according to Thum's method (*Monatsh.*, 1893, **14**, 294). As there is a risk of the acid being decomposed on keeping, most of the conductivity measurements given below were undertaken with a fresh preparation each time.

The conductivities were determined in a closed cell at 0°. The water used in these experiments had a conductivity of 0.3×10^{-6} .

Sodium Hyponitrite.

Equivalent conductivity.	Dilution.	Equivalent conductivity.	Dilution.
42.23	5.45	53.89	97.28
44.72	10.90	55.75	105.32
46.75	21.80	57.98	210.64
47.12	24.32	60.75	421.38
49.32	43.60	64.98	482.76
50.12	48.64	68.32	1685.52
51.56	87.20		

Calcium Hyponitrite.

Equivalent conductivity.	Dilution.	Equivalent conductivity.	Dilution.
64.32	110	69.12	440
65.98	150	69.89	600
66.99	220	70.93	880
67.95	300	73.12	1200

Hyponitrous Acid.

Equivalent conductivity.	Dilution.	Equivalent conductivity.	Dilution.
1.08	6.22	3.10	44.74
1.49	12.11	3.85	73.47
1.52	12.44	4.21	89.48
2.12	22.37	5.43	146.94
2.39	24.22		

The measurement of the two salts was taken in a cell in which the two electrodes were about 4 cm. apart, but in the case of the

acid it was performed in a cell in which the electrodes were about 1 cm. apart.

In calculating the mobility of natrion (Na^+) and calcion ($\frac{1}{2}\text{Ca}^{++}$) at 0° , we had to rely on the value of the temperature-coefficient of mobility as given by Kohlrausch (*Sitzungsber., K. Akad. Wiss. Berlin*, 1902, **6**, 72; 1901, **5**, 1031; also *Zeitsch. Elektrochem.*, 1908, **14**, 129). The mobility of natrion (Na^+) at 18° is 43.55. The values of α and β in the expression of Kohlrausch:

$$U_r = U_{18} [1 + \alpha(t - 18^\circ) + \beta(t - 18^\circ)^2]$$

for natrion (Na^+) are 0.245 and 0.000116. From whence we get 26.6 for the value of natrion (Na^+) at 0° .

The maximum value of the equivalent conductivity of sodium hyponitrite is found to be approximately 68, as shown in the table. This value is, however, too high, owing to hydrolysis, since hyponitrous acid is a very weak acid. Therefore, allowing for hydrolysis, the probable value for sodium hyponitrite is about 64. Subtracting from this the value for the mobility of natrion (Na^+) at 0° , we obtain the value for the mobility of hyponitrosion (NO') of 38 approximately. Similarly, the value of the mobility of calcion ($\frac{1}{2}\text{Ca}^{++}$) at 0° , deduced from Kohlrausch's expression, is 31.39. Allowing for hydrolysis, the probable value for maximum equivalent conductivity of calcium hyponitrite is about 70. Therefore the mobility of hyponitrosion at 0° as deduced from this salt becomes 38.7 approximately. Thus very probably hyponitrosion (NO') moves more slowly than nitranion (NO'_3) or nitrosion (NO'_2) (compare Rây and Dhar, this vol., p. 12).

An attempt to deduce the mobility of hyponitrosion (NO') from an electrometric investigation of a saturated solution of silver hyponitrite and from the conductivity of this solution, was unsuccessful.

Since there are no trustworthy data for the mobility of hydron (H^+) at 0° , the dissociation constant of hyponitrous acid could not be calculated. From the equivalent conductivities given in the table, however, it is evident that hyponitrous acid is weaker than acetic acid, and stronger than carbonic acid (compare Walker and Cormack, T., 1900, **77**, 5).

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CLXX.—*The Vapour Density of Ammonium Nitrate, Benzoate, and Acetate.*

By PRAFULLA CHANDRA RÂY and SARAT CHANDRA JÂNÂ.

IN continuation of the work on the vapour density of ammonium nitrite (T., 1912, 101, 1185), that of ammonium nitrate has been investigated. Preliminary trials showed that ammonium nitrate begins to sublime very slowly in a vacuum at about 180°, and as complete vaporisation of the substance requires a much higher temperature, Hofmann's method was found to be impracticable, for at a temperature much higher than 200° mercury has an appreciable vapour tension. In these circumstances, the apparatus adopted was that described by Bleier and Kohn (*Monatsh.*, 1899, 20, 505), with the difference that the outer jacket used was of iron.

Ammonium Nitrate.

The sublimation of ammonium nitrate takes place in the vacuum of the Sprengel pump at a temperature of about 180°. Since at the boiling point of nitrobenzene (208°) no appreciable vaporisation was obtained, bromobenzene (b. p. 280°) was employed in the outer jacket, the upper part of which was wrapped with cotton wool and asbestos, to diminish loss of heat by radiation.

In order to determine the constant of the apparatus—that is, the increase of pressure caused by the vaporisation of a millimolecule of substance at the temperature of the experiment—nitrobenzene (b. p. 208°), benzyl alcohol (b. p. 206°), and methyl salicylate (b. p. 224°) were chosen as standard substances. The first substance gave somewhat anomalous results, due probably to a slight charring of the substance, which could be observed when the tube was taken out after the experiment was finished. The second and the third substances, however, gave satisfactory results. As a mean of several experiments, the constant obtained was 196·7.

	Wt. in milligrams.	P. in mm.	C.
Methyl salicylate	83·4	108·5	197·7
	101·4	130·5	195·5
	96·2	121·5	192·0
Benzyl alcohol	61·6	114·0	201·0
	64·2	117·5	197·7
		Mean.....	196·7

A small tube, containing a weighed quantity of ammonium nitrate, was introduced into the apparatus, and allowed to remain at the "catch." The apparatus was then exhausted, and the

mercury in the manometer was allowed to rise to the mark. The pressure in the apparatus was nearly 80 mm. The connexion with the pump was then cut off, and the whole allowed to remain for two to three minutes to ascertain whether the mercury remained stationary at the mark. If this was so, the weighed tube was allowed to drop in by a gentle pull at the "catch." The vaporisation began in a minute, and was completed in about eight to ten minutes. The mercury level was adjusted, and it was found that in about ten to twelve minutes the thread began to rise, indicating that condensation of the products had set in. The maximum reading was therefore taken. The apparatus was then allowed to cool for some time until the temperature fell to about 90°. The products were then drawn off by the Sprengel pump and collected in a graduated tube over mercury. This gas, on analysis, was found to contain air and nitrous oxide only. Not a trace of ammonia or nitric oxide could be detected in it.

The apparatus was now disconnected. Small crystals of ammonium nitrate could be seen deposited in the cooler parts of the neck. The vaporising globe and the stem were washed with as small a quantity of water as possible. The wash-water was treated in a Crum-Frankland nitrometer. The gas produced was found to be nitric oxide. In one experiment the quantity of ammonium nitrate, corresponding with the amount of nitric oxide and nitrous oxide, was found to be 0.0185 gram, whilst the quantity actually taken was 0.0192 gram.

Calculation of the Vapour Density.—The density of the mixed gases, consisting of nitrous oxide, water vapour, and ammonium nitrate vapour, was calculated by means of the formula $d = cw/2p$. 41.4 Milligrams of ammonium nitrate produced a difference of pressure of 224 mm. The value of C was known to be 196.7, and from this the density was found to be 18.10. Now, the volume of nitrous oxide determined in the residual air from the vaporising globe was 3.05 c.c. at N.T.P.* The amount of ammonium nitrate corresponding with this volume of nitrous oxide was 10.86 milligrams from the equation: $\text{NH}_4\text{NO}_3 = 2\text{H}_2\text{O} + \text{N}_2\text{O}$.

Now, the volume of the mixed gases was found from the weight, of the substance originally taken, and the density by means of the formula $w = v \times d \times 0.000089$ g. This volume was 25.69 c.c. From this, the volume of N_2O and $2\text{H}_2\text{O}$ was deducted, and the value was 16.54 c.c. From the weight of the undecomposed ammonium nitrate, which is $(41.4 - 10.86)$ 30.54 milligrams, and the volume

* The nitrous oxide was removed by repeatedly shaking it with tap-water and changing the solvent four or five times until no more diminution in volume was noticed. Blank experiments in which mixtures of air and nitrous oxide in varying proportions were similarly treated proved the trustworthiness of this method.

occupied by it in the gaseous state, which is 16.54 c.c., we find the density to be 20.70.

The following results are calculated in a similar way from other experiments:

Weight in milligrams.	P. in mm.	Vol. of N ₂ O at N.T.P.	Weight of NH ₄ NO ₃ corresponding with N ₂ O.	Calculated density.
II. 17.4	103.5	2.321	8.26	21.08
III. 38.3	233.0	5.034	17.92	19.89
IV. 22.1	134.5	3.221	11.47	20.90
V. 95.5	537.0	9.616	33.99	21.47
VI. 37.4	206.2	2.159	7.686	19.51
VII. 39.5	200.0	1.623	5.776	21.07

As a mean of these experiments, the vapour density is found to be 20.66. It is evident, then, that at a temperature of 280° and under a pressure of 80 mm., the dissociation of ammonium nitrate is complete; a part of the salt at the same time decomposes into nitrous oxide and water.

Veley has shown that molten ammonium nitrate shows an acid reaction due to the presence of nitric acid (T., 1883, **43**, 370). This is explained by the fact that the substance decomposes into ammonia and nitric acid, but as the former diffuses off more rapidly than the latter, the molten mass acquires an acid reaction.

In order to settle this point more satisfactorily, a quantity of ammonium nitrate was placed in a glass tube, sealed at one end, in which a porous diaphragm was interposed. A strip of red litmus paper was then introduced into the drawn-out portion. This end was then connected with the Sprengel pump, and when the requisite vacuum was attained the tube was immersed in a bath of paraffin heated at about 260°, and the pump allowed to work. After a few minutes the strip became blue, and subsequently red again, showing that dissociation takes place, the ammonia diffusing more rapidly than the nitric acid.

A few experiments were conducted in which the vapour density apparatus was previously partly filled with ammonia. It was noticed that the amount of ammonium nitrate which decomposed under this condition was appreciably less. Thus, in one experiment, using 0.065 gram of the salt, we obtained only 1.8 c.c. of nitrous oxide. This is quite in agreement with the results of Veley, who found that on passing ammonia into molten ammonium nitrate, the decomposition of the substance was completely arrested (*loc. cit.*).

Ammonium Benzoate and Acetate.

Preliminary experiments showed that ammonium acetate melts at about 85° in a vacuum. It rapidly loses ammonia, which can be

collected at the end of the Sprengel pump. It can be sublimed very slowly; the greater part of it, however, undergoes dissociation, and much free acetic acid is left behind. Ammonium benzoate can be sublimed at 160° without melting. There is rapid evolution of ammonia, and a mixture of ammonium benzoate and benzoic acid is deposited. The lower part of the tube contains, however, almost pure ammonium benzoate.

For the determination of the vapour density of these substances a bath of nitrobenzene (b. p. 208°) was used. The constant of the apparatus was determined by means of benzene. The following results were obtained with ammonium benzoate:

Weight in milligrams.	<i>P</i> in millimetres.	<i>d.</i>
15.5	25	40.4
18.8	29	42.3
19.2	29	43.2
25.6	38	44.0

The theoretical value of the density for complete dissociation is 34.75. The high values obtained in the experiment are due to the fact that in each case small, feathery crystals of benzoic acid were found deposited at the neck of the tube. In order to avoid this, very small quantities of the salt were taken, but in this case the experimental errors vitiated the results, and the time required for complete vaporisation was even here long enough to allow of the deposit of some benzoic acid crystals at the neck through diffusion. The easy condensability of benzoic acid made it extremely difficult to determine the vapour density with accuracy. The above table shows that with increased quantities of the salt the value of the density increases. This is because the time required for complete vaporisation increases, and so the diffusion is greater and larger quantities of the acid are condensed at the neck.

In the case of ammonium acetate this difficulty is overcome, as the acetic acid vapour is not so easily condensable. The following table gives the result in this case:

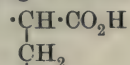
Weight in milligrams.	<i>P.</i> in min.	<i>d.</i>
65.0	208	20.4
65.8	218	19.7
89.0	289	20.1

The calculated value of the density for complete dissociation is 19.3. It is proved, therefore, that in this case also complete dissociation of the substance takes place.

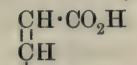
CLXXI.—*The Chemistry of the Glutaconic Acids.*
Part VIII. β -Phenylglutaconic Acid and the
 β -Phenyl- α -methylglutaconic Acids.

By JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD.

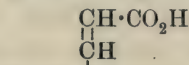
THE experiments described in the previous parts of this series have shown that a derivative of glutaconic acid containing the mobile hydrogen atom should, theoretically, exist in three forms, namely:



Normal form.



cis-Labile form.



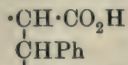
trans-Labile form.

It has been proved, moreover, that the stability of the *cis*-labile acid, on which depends the possibility of converting it into the *trans*-isomeride, is determined by the weight of the groups attached to the carbon atoms of the three-carbon system. Thus it was found possible to isolate the *trans*-modification of α -benzyl- β -methylglutaconic acid, and to show that the *cis*-isomeride, whilst incapable of a separate existence, must be present in the form of its salts (T., 1912, 101, 1739).

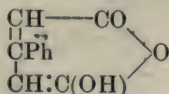
The great stability of the *cis*-labile modification of β -methylglutaconic acid (T., 1912, 101, 858), compared with that of the corresponding acid derived from α -methylglutaconic acid, showed that increased stability is conferred by the presence of the substituting group on the β -carbon atom, and it might therefore be expected that the attachment of the phenyl group to the β -carbon atom would confer increased stability on the *cis*-form of the acid thus substituted.

Unfortunately, β -phenylglutaconic acid does not lend itself to direct comparison; the acid exists in one well-defined form, which melts at 154—155°, and yields an hydroxy-anhydride, which has the abnormally high melting point of 206°. The hydroxy-anhydride when boiled with water is converted into the acid melting at 154—155°, although the presence of another acid, stable only in the form of its salts, has been clearly proved (T., 1912, 101, 861; Feist and Pomme, *Annalen*, 1909, 370, 76).

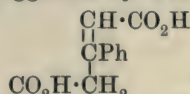
We have assigned the normal structure to the acid melting at 154—155° instead of the *trans*-structure, as suggested by Feist:



Normal form.



Hydroxy-anhydride.



trans-Form (Feist).

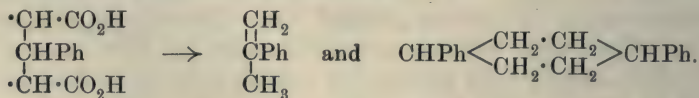
because the acid is readily converted into the hydroxy-anhydride by cold acetyl chloride, and also because numerous experiments have failed to yield the normal anhydride, showing that the hydrogen atom is still mobile within the molecule of β -phenylglutaconic acid.

On the other hand, the acid melting at $154\text{--}155^\circ$ is unaltered by prolonged boiling with concentrated alkali hydroxide, and is not apparently converted under these conditions into the alkali salt of the *cis*-labile acid; in this respect, therefore, it differs markedly from the normal modification of β -methylglutaconic acid, which is completely converted into the salt of the *cis*-modification under the same experimental conditions.

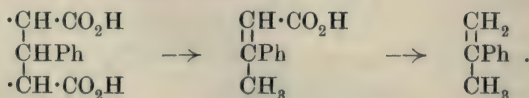
It must be remembered, however, that the *cis*-labile forms of acids of this series are frequently so unstable that the mere act of liberating them from their salts by the aid of mineral acids is sufficient to transpose them into their more stable normal modifications. That this is actually the case with the *cis*-labile form of β -phenylglutaconic acid is shown by the fact that it is only possible to prove that the alkali salt of the unstable *cis*-labile modification is formed by the action of alkali on the hydroxy-anhydride in the presence of casein by decomposing the corresponding silver salt with hydrogen sulphide; if the alkali salt is acidified by mineral acids, the normal form, melting at $154\text{--}155^\circ$, is at once precipitated.

Indirect proof that the sodium salt of the unstable *cis*-labile modification of β -phenylglutaconic acid is formed by the action of aqueous sodium hydroxide on the normal acid is supplied by the following series of experiments.

When normal β -phenylglutaconic acid is boiled with dilute hydrochloric or sulphuric acids, it is rapidly transformed into carbon dioxide and two hydrocarbons, one of which is *isopropenyl*-benzene, and the other, with twice this molecular weight, which is probably 1:4-diphenylcyclohexane:

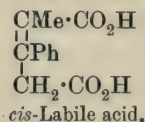
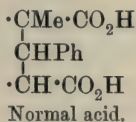
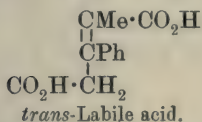


Boiling water is without action on β -phenylglutaconic acid, but in a sealed tube at 160° transformation into *isopropenyl*benzene is complete. β -Methylcinnamic acid can be isolated as an intermediate product in this reaction:



When, however, β -phenylglutaconic acid is heated with excess of aqueous alkali, even in a sealed tube at a high temperature, it is recovered unchanged on acidifying. It follows therefore that the alkali salt of the normal acid is transformed into the stable sodium salt of the *cis*-labile acid. This seems to be the only possible explanation, since it is well known that the presence of excess of alkali favours the elimination of carbon dioxide from acids of this type.

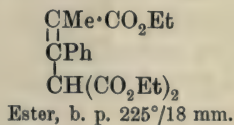
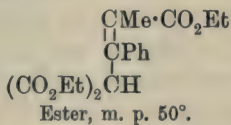
In the hope of throwing further light on this question, we have prepared β -phenyl- α -methylglutaconic acid, and have, for the first time, succeeded in isolating a derivative of glutaconic acid, containing the mobile hydrogen atom, in three distinct forms, which are without doubt the normal, *cis*-labile, and *trans*-labile modifications, formulated thus:



The ester from which these acids can be derived can be isolated in two forms by the action of methyl iodide on the sodium derived, which is produced in the condensation of ethyl phenylpropiolate and ethyl sodiomalonate (T., 1912, 101, 868):



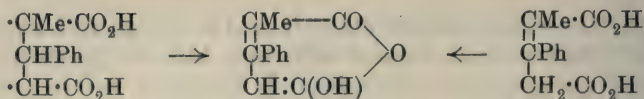
It is probable that, in this ester, the mobility of the hydrogen atom ceases, and that the two forms represent true *cis*- and *trans*-modifications, thus:



Support is given to this view from the fact that the solid ester yields the *trans*-labile acid only, under conditions of hydrolysis, which convert the liquid ester into a mixture of the normal and *cis*-labile acids. Neither form of the ester is converted into a sodium derivative by alcoholic sodium ethoxide.

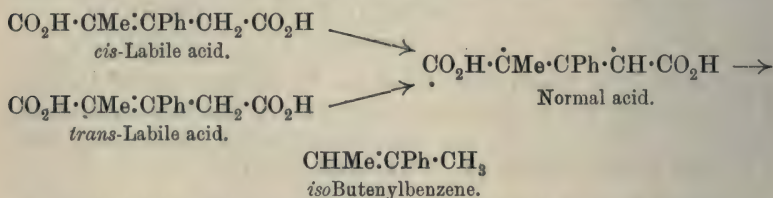
The dibasic acids derived from these esters can be separated by means of the barium salts in the manner described in the experimental portion.

The *trans*-labile acid melts at 155°, and is quite unaltered, even on prolonged boiling, by acetyl chloride. The normal acid melts at 120°, and the *cis*-labile acid at 108°; both are readily converted into the hydroxy-anhydride (m. p. 94°) by acetyl chloride:



When the hydroxy-anhydride is boiled with water, it yields the normal acid melting at 120° ; when hydrolysed by strong alkali, it is transformed into an alkali salt, from which acids precipitate a mixture of the normal acid and the *cis*-labile acid. When hydrolysed by dilute alkali in the presence of casein, and the acid isolated through the silver salt and hydrogen sulphide, the *cis*-labile acid melting at 108° is the sole product.

All three forms eliminate carbon dioxide when boiled with dilute hydrochloric or sulphuric acids, and pass into *isobutenylbenzene*, but this decomposition evidently takes place through the normal form alone, because, if the reaction in the cases of the *trans*- and *cis*-labile acids is stopped before completion, the dibasic acid remaining unaltered is always the normal acid melting at 120° :



It was not found possible to convert either the *cis*-labile acid or the normal acid into the *trans*-labile acid, and it would appear as if this acid can only be produced by the hydrolysis of the *trans*-tricarboxylic ester in the manner already mentioned. This point is of some interest, because it follows that if similar esters could be isolated in the case of other members of the series, it should be possible to prepare other *trans*-acids of similar type. It shows, moreover, that the view expressed in an earlier communication, namely, that the isolation of the *trans*-forms is prevented by the fact that in order to prepare them it is necessary to pass through the more stable normal form is correct.

The *trans*-labile acid is converted into the alkali salt of the *cis*-labile acid on prolonged boiling with alkali hydroxide, and from this alkali salt a mixture of the normal acid and the *cis*-labile acid is obtained on acidifying.

EXPERIMENTAL.

(1) *The Decomposition of β -Phenylglutaconic Acid.*

(a) *isoPropenylbenzene*, $C_6H_5 \cdot CMe:CH_2$, and *1:4-Diphenylcyclohexane*.

These substances are formed when β -phenylglutaconic acid is boiled with either 10 per cent. aqueous sulphuric acid or 15 per cent. aqueous hydrochloric acid, and can be isolated by distillation in a current of steam; 10 grams of the acid, when boiled with 100 c.c. of the dilute mineral acid, are completely decomposed in the course of three hours.

The two hydrocarbons are then separated by fractional distillation. *isoPropenylbenzene* boils at $164^\circ/749$ mm.:

0.1362 gave 0.4543 CO_2 and 0.1048 H_2O . $C=91.18$; $H=8.55$.

C_9H_{10} requires $C=91.5$; $H=8.5$ per cent.

3.08 Grams decolorised 4.09 grams of bromine in chloroform solution. $C_9H_{10} + Br_2$ requires 4.17 grams.

Although no definite derivatives of this hydrocarbon could be prepared, there can be no doubt that it is identical with the substance obtained by Klages (*Ber.*, 1902, **35**, 2640), Tiffeneau (*Compt. rend.*, 1902, **135**, 845), and by Matsubara and Perkin (*T.*, 1905, **87**, 672) from phenyldimethylcarbinol.

1:4-Diphenylcyclohexane boils at $190^\circ/29$ mm. as a colourless, mobile liquid:

0.1523 gave 0.5115 CO_2 and 0.1154 H_2O . $C=91.58$; $H=8.42$.

$C_{18}H_{20}$ requires $C=91.5$; $H=8.5$ per cent.

Bromine in chloroform solution acts on the hydrocarbon at the ordinary temperature with the formation of hydrogen bromide; no definite derivatives have as yet been isolated, and the compound is still under investigation.

(b) *β -Methylcinnamic Acid*, $C_6H_5 \cdot CMe:CH \cdot CO_2H$, and *isoPropenylbenzene*.

A mixture of these substances is produced when β -phenylglutaconic acid is heated in a sealed tube with water at 160° for six hours, although the amount of the hydrocarbon formed under these conditions is very small.

A larger yield of the unsaturated hydrocarbon unmixed with diphenylcyclopropane can be obtained by heating the sodium hydrogen salt with water at 160° for seven hours. In either case the hydrocarbon was isolated by distillation in steam, and the residual acid recrystallised from dilute alcohol. β -Methylcinnamic

acid melts at 97° . (Found, $C=73.69$; $H=6.19$. $C_{10}H_{10}O_2$ requires $C=74.1$; $H=6.2$ per cent.)

The acid has been prepared by G. Schroeter (*Ber.*, 1904, **37**, 1092; 1907, **40**, 1593). It was characterised by the formation of the dibromide of the dimethyl ester, $C_6H_5 \cdot CMeBr \cdot CHBr \cdot CO_2Me$, melting at $78-79^{\circ}$. (Found, $Br=47.53$. Calc., $Br=47.6$ per cent.)

(c) When the disodium salt of β -phenylglutaconic acid is heated with water in a sealed tube at 160° for ten hours, a small quantity of the unsaturated hydrocarbon and β -methyleinnamic acid can be isolated from the product. When an excess of sodium hydroxide is present, the sodium salt of β -phenylglutaconic acid can be heated for twenty hours at 160° , and the acid is recovered unaltered when the product is acidified.

(2) *The cis- and trans-forms of Ethyl α -Carbethoxy- β -phenyl- α -methylglutaconate, $CO_2Et \cdot CMe \cdot CPh \cdot CH(CO_2Et)_2$.*

The yellow sodium compound which is formed by the interaction of ethyl phenylpropiolate and ethyl sodiomalonate (T., 1912, **101**, 868) is converted into a mixture of these esters when it is boiled, in alcoholic solution, with excess of methyl iodide. The reaction is finished when the yellow colour of the solution has been discharged, and the product is isolated in the usual way. The mixed esters boil at $225^{\circ}/18$ mm., and the distillate slowly deposits crystals. These were collected after some months, and recrystallised from light petroleum, when the large, colourless prisms of the *trans*-form, melting at 50° , were obtained:

0.1520 gave 0.3637 CO_2 and 0.0930 H_2O . $C=65.26$; $H=6.80$.

$C_{19}H_{24}O_6$ requires $C=65.5$; $H=6.9$ per cent.

For practical purposes the separation of the solid ester can be completed in the course of a day if the mixed esters are dissolved in an equal volume of light petroleum and the solution is placed in a mixture of ice and salt.

The *trans*-modification is readily soluble in all organic solvents excepting light petroleum. It boils at $225^{\circ}/18$ mm. as a viscid liquid, which quickly solidifies on cooling.

The *cis*-modification distils at the same temperature as its *trans*-isomeride, but cannot be obtained in the solid condition:

0.1507 gave 0.3626 CO_2 and 0.0913 H_2O . $C=65.61$; $H=6.73$.

$C_{19}H_{24}O_6$ requires $C=65.5$; $H=6.9$ per cent.

trans-Labile β -Phenyl- α -methylglutaconic Acid,
 $\text{CO}_2\text{H} \cdot \text{CMe} \cdot \text{CPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}.$

This acid is formed by the hydrolysis of the *trans*-modification of the tricarboxylic ester by means of slightly more than the calculated quantity of alcoholic potassium hydroxide, and is precipitated on acidifying the aqueous solution freed from alcohol. Care must be taken to stop the hydrolysis so soon as completed, otherwise some of the *trans*-potassium salt will be converted into the potassium salt of the *cis*-labile acid by the excess of alkali present. In order to avoid this, it is advisable to remove the excess of alcohol, as far as possible, in a vacuum desiccator at the ordinary temperature, and not on the water-bath. The acid crystallises from hot water in well-defined needles, which melt at 155° :

0.1833 gave 0.4400 CO_2 and 0.0889 H_2O . $\text{C} = 65.46$; $\text{H} = 5.39$.

$\text{C}_{12}\text{H}_{12}\text{O}_4$ requires $\text{C} = 65.5$; $\text{H} = 5.5$ per cent.

The acid is unaltered on prolonged boiling with acetyl chloride, but is slowly converted into the hydroxy-anhydride (see next paragraph) when heated in a sealed tube at 100° with this reagent.

The barium salt is soluble in water, and in this way the acid can be readily distinguished from β -phenylglutaconic acid (m. p. 154 — 155°), the barium salt of which is insoluble in water.

Normal β -Phenyl- α -methylglutaconic Acid,
 $\text{CO}_2\text{H} \cdot \text{CMe} \cdot \text{CPh} \cdot \text{CH} \cdot \text{CO}_2\text{H}.$

This acid can be formed either by the action of aqueous alkali on the *trans*-labile acid (see later), or by the hydrolysis of the *cis*-tricarboxylic ester by means of alcoholic potassium hydroxide. In both cases a mixture of the normal acid and the *cis*-labile acid is precipitated when the product is acidified, and can be separated through the agency of the barium salts.

The separation is effected in the following manner. The mixed acids are converted into a neutral solution of the ammonium salts, and the solution is boiled with an aqueous solution containing a slight excess of barium chloride. The mixed barium salts, after being washed with boiling water, are repeatedly extracted with cold water. The *barium* salt of the normal acid is soluble in cold water, but is precipitated in the crystalline condition when the solution is boiled; it again dissolves when the liquid is cooled:

0.6247 gave 0.4090 BaSO_4 . $\text{Ba} = 38.49$.

$\text{C}_{12}\text{H}_{10}\text{O}_4\text{Ba}$ requires $\text{Ba} = 38.59$ per cent.

The acid is precipitated when the solution of the barium salt is acidified with excess of hydrochloric acid; it can be recrystallised

either from hot water or benzene, and forms small, colourless needles, which melt at 120° , and evolve water vapour at 130° :

0.2163 gave 0.5182 CO_2 and 0.1062 H_2O . $\text{C}=65.34$; $\text{H}=5.46$.

0.1685 „ 0.4044 CO_2 „ 0.0816 H_2O . $\text{C}=65.45$; $\text{H}=5.38$.

$\text{C}_{12}\text{H}_{12}\text{O}_4$ requires $\text{C}=65.5$; $\text{H}=5.5$ per cent.

The acid is at once attacked by acetyl chloride, yielding the hydroxy-anhydride.

A curious *barium hydrogen* salt is precipitated if the solution of the barium salt described above is acidified with dilute hydrochloric acid. It crystallises from hot water in feathery needles:

0.3073 gave 0.0893 BaSO_4 . $\text{Ba}=17.09$.

$(\text{C}_{12}\text{H}_{11}\text{O}_4)_2\text{Ba}, 12\text{H}_2\text{O}$ requires $\text{Ba}=17.1$ per cent.

The salt is stable at 100° , and, as heating at a higher temperature leads to decomposition, the presence of the water of crystallisation could not be proved. The aqueous solution of the salt is acid to litmus, and when treated with concentrated hydrochloric acid, the acid melting at 120° is precipitated.

cis-Labile β -Phenyl- α -methylglutaconic Acid,
 $\text{CO}_2\text{H} \cdot \text{CMe} \cdot \text{CPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$.

The *barium* salt of this acid is insoluble in cold water, and therefore remains after the barium salt of the normal acid has been extracted. It was purified by conversion into the acid, which was again transformed into the barium salt, only, in this case, the salt was precipitated in the cold:

0.3572 gave 0.2341 BaSO_4 . $\text{Ba}=38.54$.

$\text{C}_{12}\text{H}_{10}\text{O}_4\text{Ba}$ requires $\text{Ba}=38.6$ per cent.

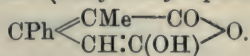
The acid, formed from the barium salt by means of concentrated hydrochloric acid, separates from benzene in small, colourless prisms, which melt at 108° , passing into the hydroxy-anhydride at a few degrees above this temperature:

0.1702 gave 0.4084 CO_2 and 0.0825 H_2O . $\text{C}=65.44$; $\text{H}=5.39$.

$\text{C}_{12}\text{H}_{12}\text{O}_4$ requires $\text{C}=65.5$; $\text{H}=5.5$ per cent.

The acid is quickly attacked by acetyl chloride even at the ordinary temperature.

The Hydroxy-anhydride (6-Hydroxy-4-phenyl-3-methyl-2-pyrone),



This substance is formed by the action of acetyl chloride on either the normal acid or the *cis-labile* acid at the temperature of the boiling reagent, and can be obtained as a white solid on

evaporating the excess of chloride in an exhausted desiccator over potassium hydroxide.

The compound crystallises from a mixture of benzene and light petroleum in small, colourless needles, which melt at 94° :

0.1834 gave 0.4791 CO_2 and 0.0847 H_2O . $\text{C}=71.24$; $\text{H}=5.13$.

$\text{C}_{12}\text{H}_{10}\text{O}_3$ requires $\text{C}=71.3$; $\text{H}=5.0$ per cent.

The anhydride is readily soluble in benzene, and gives a blue colour in alcoholic solution with ferric chloride. It is soluble in aqueous solutions of alkali carbonate, forming a yellow solution:

0.2176 required 5.4 c.c. NaOH -solution (1 c.c. = 0.0079 gram NaOH).

$\text{C}_{12}\text{H}_{10}\text{O}_3$ (monobasic) requires 5.45 c.c.

The *conversion of the hydroxy-anhydride into the acid melting at 120°* is effected by boiling with water until complete solution is obtained. The pure acid separates on cooling. The *conversion into a mixture of the acids melting at 120° and at 108°* is effected by allowing a solution of the hydroxy-anhydride in concentrated alkali hydroxide to remain at the ordinary temperature until its yellow colour has been completely discharged. The mixed acids, precipitated on acidifying, can then be separated by means of their barium salts in the manner already described. The *conversion into the acid melting at 108°* can be brought about by the aid of casein and $N/10$ -sodium carbonate in the manner described for the hydroxy-anhydride of β -phenylglutaconic acid (Feist and Pomme, *Annalen*, 1909, **370**, 76), the acid being isolated through the silver salt, which was decomposed by hydrogen sulphide. The acid melting at 108° was the sole product.

The *semianilide*, $\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{CMe}\cdot\text{CO}_2\text{H}$, from a benzene solution of the hydroxy-anhydride and aniline, crystallises from benzene in small, colourless prisms, which melt at 143° :

0.1923 gave 0.5155 CO_2 and 0.1016 H_2O . $\text{C}=73.10$; $\text{H}=5.87$.

$\text{C}_{18}\text{H}_{17}\text{O}_3\text{N}$ requires $\text{C}=73.2$; $\text{H}=5.8$ per cent.

The semianilide is soluble in alkali carbonates, and is transformed into the hydroxyanil at 160° .

The Hydroxyanil (3-Hydroxy-2:5-diphenyl-6-methyl-1:2-dihydropyridone), $\text{CPh}\begin{matrix} \text{CMe} \text{---} \text{CO} \\ \text{CH:C(OH)} \end{matrix} \text{NPh}$.

This compound can be prepared either by heating the above semianilide or from either one of the three isomeric acids, by heating it with a molecular amount of aniline at 170° for fifteen minutes. It can be isolated by rubbing the product with dry ether, and can be obtained in small, pale yellow needles, melting at 216° , by recrystallisation from alcohol:

0.1486 gave 0.4246 CO_2 and 0.0752 H_2O . $\text{C}=77.93$; $\text{H}=5.62$.

$\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}$ requires $\text{C}=78.0$; $\text{H}=5.4$ per cent.

The compound dissolves in aqueous solutions of alkali carbonates, and is precipitated unchanged when the solution is acidified:

0.2872 required 5.2 c.c. NaOH -solution (1 c.c. = 0.0079 gram NaOH).

$\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}$ (monobasic) requires 5.25 c.c.

The Decomposition of the β -Phenyl- α -methylglutaconic Acids.

(a) *isoButenylbenzene*, $\text{C}_6\text{H}_5\cdot\text{CMe}\cdot\text{CHMe}$.—This hydrocarbon is formed from either one of the three isomerides when it is boiled with dilute hydrochloric or sulphuric acids until carbon dioxide ceases to be evolved, and can be isolated by distillation in a current of steam. It is mobile liquid, having an odour resembling that of petroleum, and boils at $169^\circ/750$ mm.:

0.2013 gave 0.6702 CO_2 and 0.1668 H_2O . $\text{C}=90.81$; $\text{H}=9.21$.

$\text{C}_{10}\text{H}_{12}$ requires $\text{C}=90.9$; $\text{H}=9.1$ per cent.

Only a trace of a liquid of higher boiling point is formed in this reaction, which was too small for investigation. It is evident therefore that the hydrocarbon corresponding with diphenylcyclohexane is not formed under these conditions.

isoButenylbenzene readily forms a dibromide with bromine in chloroform solution, but the compound eliminates hydrogen bromide on distillation, and no definite boiling point could be obtained:

2.56 grams decolorised 3.11 grams of bromine.

$\text{C}_{10}\text{H}_{12} + \text{Br}_2$ requires 3.10 grams.

Experiments were made in which the action of the mineral acid was stopped before the conversion into the hydrocarbon was complete. In the case of the acids melting at 155° and at 108° , the unchanged acid was found to be the normal form, melting at 120° . The residue in the case of the normal acid was found to be unaltered acid. It follows therefore that the *trans*-labile acid and the *cis*-labile acid are converted into the normal acid prior to yielding the hydrocarbon.

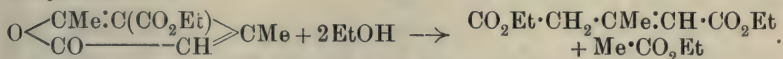
(b) The disodium salt of the *cis*-labile acid, produced either by the action of alkali on the normal and *trans*-labile modifications or from the *cis*-labile acid itself, is unaltered when heated in a sealed tube with excess of alkali for ten hours at 170° . Attempts to prepare dimethylcinnamic acid from the sodium hydrogen salt have not as yet been successful.

THE SORBY RESEARCH LABORATORY,
THE UNIVERSITY, SHEFFIELD.

CLXXII.—*The Chemistry of the Glutaconic Acids.*
Part IX. A Method for Distinguishing Between
the Esters of the Normal and Labile Acids.

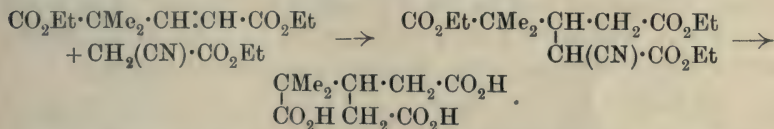
By JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD.

IN Part V of this series (T., 1912, **101**, 1565) a method was described by which the *cis*-labile ester of β -methylglutaconic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, could be prepared in a yield of 75 per cent. by the action of alcoholic sodium ethoxide on ethyl *iso*-dehydracetate:



The ester of the normal acid, $\text{CO}_2\text{H}\cdot\dot{\text{C}}\text{H}\cdot\text{CHMe}\cdot\dot{\text{C}}\text{H}\cdot\text{CO}_2\text{H}$, can also be easily prepared by the esterification of the normal acid, and it is therefore a simple matter to obtain large quantities of these esters for the purpose of comparison.

It has been shown by Perkin (T., 1902, **81**, 246) that the ester of a substituted glutaconic acid in which the unsaturated structure is fixed, condenses with the sodium derivative of ethyl cyanoacetate to form a condensation product, for in this way he was enabled to synthesise *isocamphoronic* acid by condensing ethyl $\alpha\alpha$ -dimethylglutaconate with ethyl sodiocyanoacetate and hydrolysing the cyano-ester formed:

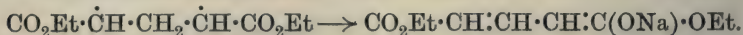


It is therefore to be expected that the esters of the labile acids would react in the same manner with the sodium compound of ethyl cyanoacetate to form a cyano-ester, which would hydrolyse to a homologue of *isocamphoronic* acid. On the other hand, if the structure of the esters of the normal acid is analogous to that of ethyl *isophthalate* (T., 1912, **101**, 871), it is to be expected that they would not enter into condensation with additive substances of the type of ethyl cyanoacetate.

Before investigating the two esters of β -methylglutaconic acid, it was thought advisable to experiment with several esters of the normal acids of this series in order to ascertain the extent to which they were capable of forming additive products, the first substance treated being ethyl glutaconate.

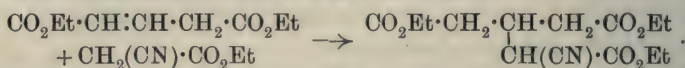
Glutaconic acid is certainly the most mobile acid of the series,

for although the normal acid is the only isolable form, the mobile hydrogen readily passes out of the three-carbon system, as is shown by the formation of the hydroxy-anhydride, as also by the formation of the yellow sodium derivative of the ester by the action of alcoholic sodium ethoxide:



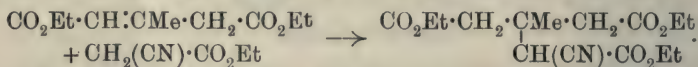
Both the yellow sodium derivative and the hydroxy-anhydride revert to the normal form on treatment with water, but it is to be expected that the amount of condensation product formed from ethyl glutaconate and ethyl sodiocyanoacetate would depend on the tendency for the ester to pass into the labile form under the experimental conditions employed.

Actually, under the experimental conditions which were subsequently found to give a yield of 60 per cent. in the case of a true labile ester, ethyl glutaconate was found to react to the extent of 5 per cent., in accordance with the scheme:



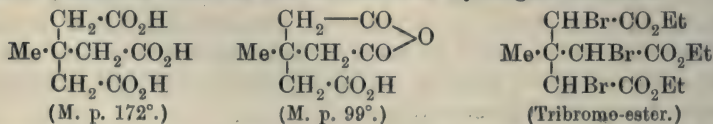
The esters of normal α -methylglutaconic acid, normal α -ethylglutaconic acid, and normal α -benzylglutaconic acid were then tried, but no trace of condensation product could be isolated, and it is therefore evident that the normal esters, as such, do not form additive products.

A comparison was then made between the ester of normal β -methylglutaconic acid and that of the *cis*-labile acid, when it was found that, whereas the last-named formed a condensation product to the extent of 60 per cent., in accordance with the scheme:



no condensation product could be isolated in the case of the normal ester.

$\beta\beta$ -Dimethylpropanetricarboxylic acid, which is formed from this cyano-ester on hydrolysis, belongs to a series of which only one or two members are at present known. The acid readily yields an anhydro-acid, and the bromination of either the acid or the anhydro-acid leads to the formation of a tribromo-ester, from which quinoline removes the elements of hydrogen bromide:



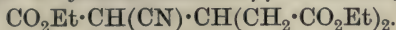
The bromine-free product appears to belong to a new system

of ring compounds, and, as it is an easy matter to prepare large quantities of $\beta\beta$ -dimethylpropanetricarboxylic acid, experiments on the structure of this and similar compounds are in progress.

EXPERIMENTAL.

Condensation of Ethyl Glutaconate and Ethyl Sodicyanoacetate.—

Ethyl α -Cyanoisobutane- $\alpha\gamma\gamma'$ -tricarboxylate,



In effecting this condensation, 28 grams of ethyl cyanoacetate were converted into the sodium compound by the aid of 5.8 grams of sodium dissolved in 70 grams of alcohol, and mixed with 46 grams of ethyl glutaconate, the mixture being heated on the water-bath for six hours. The product, worked up in the usual way, yielded a neutral ester boiling at $208^\circ/28$ mm., mixed with much unchanged ethyl glutaconate:

0.2304 gave 0.4708 CO_2 and 0.1446 H_2O . $\text{C}=55.73$; $\text{H}=6.98$.

$\text{C}_{14}\text{H}_{21}\text{O}_6\text{N}$ requires $\text{C}=56.2$; $\text{H}=7.0$ per cent.

The yield of pure ester was only about 3 grams. A considerable quantity of acid ester was isolated from the mother liquors, and this was esterified by alcohol and sulphuric acid, and the neutral ester distilled. It consisted for the most part of ethyl glutaconate, but contained a small quantity of the ester boiling at $208^\circ/28$ mm., mixed with a substance of higher boiling point. It was noticed that the neutral ester always possessed a fine blue colour, which disappeared during distillation.

isoButane- $\alpha\gamma\gamma'$ -tricarboxylic Acid, $\text{CH}(\text{CH}_2 \cdot \text{CO}_2\text{H})_3$.

The cyano-ester is best hydrolysed by dissolving it in an equal volume of concentrated sulphuric acid, adding sufficient water to keep the solution clear, and then boiling for two hours. The acid is extracted by ether, and the ethereal residue allowed to crystallise. The acid crystallises from dry ether in small, colourless prisms, which melt at 115° :

0.1694 gave 0.2740 CO_2 and 0.0819 H_2O . $\text{C}=44.12$; $\text{H}=5.37$.

$\text{C}_7\text{H}_{10}\text{O}_6$ requires $\text{C}=44.2$; $\text{H}=5.3$ per cent.

The acid is readily soluble in water and in concentrated hydrochloric acid. It reacts with acetyl chloride, forming an anhydro-acid, which could not be obtained crystalline; the quantity at our disposal was too small for further investigation.

An acid of this formula has been prepared by Coutelle (*J. pr. Chem.*, 1906, [ii], **73**, 49) by the action of chloroform on ethyl sodiomalonate. It is described as an acid, difficult to purify, which

melts at about 95°. Coutelle's acid was characterised by the formation of a barium salt of the formula $C_{14}H_{14}O_{12}Ba_3 \cdot 4H_2O$, which was precipitated from its aqueous solution by the addition of alcohol. The acid prepared by us behaves in the same manner (Found, Ba = 48.05. $C_{14}H_{14}O_{12}Ba_3$ requires Ba = 48.0 per cent.), and it is therefore probable that the two acids are identical.

Normal Ethyl α -Methylglutaconate, $CO_2Et \cdot \dot{C}H \cdot CH_2 \cdot \dot{C}Me \cdot CO_2Et$.—Normal α -methylglutaconic acid (m. p. 145—146°) is readily transformed into the above ester by esterification with alcohol and sulphuric acid. It is a mobile liquid, boiling at 165°/60 mm.:

0.1897 gave 0.4173 CO_2 and 0.1380 H_2O . C = 59.98; H = 8.08.

$C_{10}H_{16}O_4$ requires C = 60.0; H = 8.0 per cent.

Twenty grams of this ester were treated with ethyl sodiocyanoacetate under the same conditions as in the experiment with ethyl glutaconate, but no condensation product was formed.

Normal Ethyl α -Ethylglutaconate, $CO_2Et \cdot \dot{C}H \cdot CH_2 \cdot \dot{C}Et \cdot CO_2Et$.—This ester, prepared from normal α -ethylglutaconic acid (m. p. 133—134°) by esterification with alcohol and sulphuric acid, is a mobile liquid, boiling at 171°/62 mm.:

0.1939 gave 0.4383 CO_2 and 0.1495 H_2O . C = 61.65; H = 8.57.

$C_{11}H_{18}O_4$ requires C = 61.7; H = 8.4 per cent.

This ester yields no condensation product with ethyl sodiocyanoacetate.

Ethyl α -benzylglutaconate has already been described (T., 1912, 101, 886). It was prepared by the elimination of a carbethoxy-group from ethyl carbethoxy- α -benzylglutaconate by the action of alcoholic sodium ethoxide, and on account of its mode of formation was regarded as a mixture of the normal and labile esters.

An experiment with 28 grams of this ester, 11.3 grams of ethyl cyanoacetate, and 2.3 grams of sodium in alcohol yielded about 1 gram of a product, boiling at 253°/20 mm., which is evidently ethyl α -cyano- γ -benzylisobutane- $\alpha\gamma\gamma'$ -tricarboxylate,

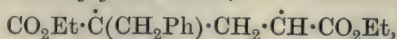


0.2103 gave 0.4982 CO_2 and 0.1331 H_2O . C = 64.61; H = 7.03.

$C_{21}H_{27}O_6N$ requires C = 64.8; H = 6.9 per cent.

The ester is a viscid oil, which is hydrolysed by dilute sulphuric acid, but the amount at our disposal was too small to enable us to isolate the acid in a pure condition.

Normal ethyl α -benzylglutaconate,



is formed in a pure condition by the esterification of normal

α -benzylglutaconic acid by means of alcohol and sulphuric acid. It is a mobile oil, which boils at $181^{\circ}/21$ mm.:

0.1934 gave 0.4923 CO_2 and 0.1255 H_2O . $\text{C}=69.41$; $\text{H}=7.21$.

$\text{C}_{16}\text{H}_{20}\text{O}_4$ requires $\text{C}=69.6$; $\text{H}=7.2$ per cent.

This ester does not form any trace of a condensation product with ethyl cyanoacetate.

Condensation of Labile Ethyl β -Methylglutaconate with Ethyl Sodicyanoacetate.—Ethyl α -Cyano- $\beta\beta$ -dimethylpropanetricarboxylate, $\text{CO}_2\text{Et}\cdot\text{CH}(\text{CN})\cdot\text{CMe}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$.

Ethyl β -methylglutaconate (84 grams) (for preparation, see T., 1912, 101, 1565) are added to the sodium compound of ethyl cyanoacetate prepared from 47 grams of the ester and 9.7 grams of sodium dissolved in 110 grams of alcohol, and the mixture is heated on the water-bath for six hours. The product consisted of about equal proportions of an acid and a neutral ester, which were separated by aqueous sodium carbonate in the usual manner. The neutral ester boiled at $210^{\circ}/21$ mm. as a moderately viscid liquid:

0.1913 gave 0.4039 CO_2 and 0.1274 H_2O . $\text{C}=57.58$; $\text{H}=7.40$.

$\text{C}_{15}\text{H}_{23}\text{O}_6\text{N}$ requires $\text{C}=57.5$; $\text{H}=7.4$ per cent.

Although the acid ester evolved carbon dioxide on being heated, so much decomposition ensued that it was found advisable, in order to purify this substance, to esterify it by means of alcohol and sulphuric acid, and fractionate the neutral ester formed. In this way a further large amount of the cyano-ester was obtained.

Ethyl α -cyano- $\beta\beta$ -dimethylpropanedicarboxylate,

$\text{CN}\cdot\text{CH}_2\cdot\text{CMe}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$,

can be prepared by the distillation of the acid ester. It is a fairly mobile liquid, which boils at $181^{\circ}/22$ mm.:

0.1976 gave 0.4326 CO_2 and 0.1419 H_2O . $\text{C}=59.69$; $\text{H}=7.98$.

$\text{C}_{12}\text{H}_{19}\text{O}_4\text{N}$ requires $\text{C}=59.8$; $\text{H}=7.9$ per cent.

$\beta\beta$ -Dimethylpropanetricarboxylic Acid, $\text{CMe}(\text{CH}_2\cdot\text{CO}_2\text{H})_3$.

Either one of the above cyano-esters is converted into this acid on hydrolysis with dilute sulphuric acid, care being taken to allow the mixture of equal volumes of ester and concentrated acid to remain for one hour prior to being diluted with an equal volume of water and boiled until the hydrolysis is completed. The acid crystallises from the solution on cooling, but is best extracted by ether; it was recrystallised, for analysis, from dry ether:

0.1965 gave 0.3394 CO_2 and 0.1052 H_2O . $\text{C}=47.10$; $\text{H}=5.95$.

$\text{C}_8\text{H}_{12}\text{O}_6$ requires $\text{C}=47.1$; $\text{H}=5.9$ per cent.

Large quantities of the acid are best recrystallised by dissolving

in water and adding an equal volume of concentrated hydrochloric acid, when the characteristic branching needles, melting at 172° , are obtained. The acid is sparingly soluble in dry ether or benzene. Unlike *isocamphoronic* acid, it is unaltered by concentrated sulphuric acid at 100° . The *silver* salt is a white, microcrystalline powder:

0.2735 gave 0.1684 Ag. Ag = 61.57.

$C_8H_9O_6Ag_3$ requires Ag = 61.7 per cent.

From a neutral solution of the ammonium salt, the calcium salt is precipitated as a white, insoluble powder; the barium salt is soluble, but is precipitated by the addition of alcohol as a gelatinous mass; the lead salt is a heavy, white precipitate, and the copper salt separates as an insoluble, green, crystalline mass.

The *anhydro-acid*, $CO_2H \cdot CH_2 \cdot CMe \cdot \begin{smallmatrix} CH_2 \cdot CO \\ CH_2 \cdot CO \end{smallmatrix} O$, is best prepared by heating the acid in an open tube at 200° until water vapour ceases to be evolved. It separates from benzene in large plates, which melt at 99° :

0.2666 gave 0.5051 CO_2 and 0.1310 H_2O . C = 51.66; H = 5.46.

$C_8H_{40}O_5$ requires C = 53.6; H = 5.4 per cent.

The *anhydro-acid* is sparingly soluble in dry ether; when boiled with water, it is converted into the acid from which it was derived.

The *double anhydride*, $(O \cdot \begin{smallmatrix} CO \cdot CH_2 \\ CO \cdot CH_2 \end{smallmatrix} \cdot CMe \cdot CH_2 \cdot CO)_2 O$.—This curious compound is formed in small amount when the acid is treated with excess of acetyl chloride for three hours at the temperature of the boiling reagent, and can be isolated from the *anhydro-acid*, which is formed at the same time, by treating the product, freed from acetyl chloride, with aqueous sodium hydrogen carbonate. The *anhydride* crystallises from ethyl acetate in small needles, which melt and decompose at 185° :

0.2131 gave 0.4221 CO_2 and 0.1003 H_2O . C = 54.01; H = 5.23.

$C_{16}H_{18}O_9$ requires C = 54.2; H = 5.1 per cent.

The *double anhydride* is sparingly soluble in all organic solvents excepting ethyl acetate; when boiled with water it is transformed into the acid melting at 172° .

The Aniline Derivatives of $\beta\beta$ -Dimethylpropanetricarboxylic Acid.

The action of aniline on a benzene solution of the *anhydro-acid* leads to the formation of an oily substance, which could not be obtained in a crystalline condition. The acid may, however, be readily characterised by the formation of two aniline derivatives which are produced when it is heated with aniline. The acid

(2 grams) is heated with three molecular proportions of aniline (2·9 grams) at 180° until water vapour ceased to be evolved. The product was then rubbed with dry ether, and the solid collected. It was found to consist of two substances, which could be readily separated by boiling alcohol.

The *anil-anilide*, $\text{NPh} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} \text{NPh}$, is insoluble in boiling alcohol. It crystallises from dilute acetic acid in small, colourless prisms, which melt at 220°:

0·1755 gave 0·4560 CO_2 and 0·0952 H_2O . $\text{C} = 70\cdot87$; $\text{H} = 6\cdot03$.

$\text{C}_{20}\text{H}_{20}\text{O}_3\text{N}_2$ requires $\text{C} = 71\cdot4$; $\text{H} = 6\cdot0$ per cent.

The *trianilide*, $\text{CMe}(\text{CH}_2 \cdot \text{CO} \cdot \text{NPh})_3$, is soluble in hot alcohol, and crystallises from this solvent in small, colourless needles, which melt at 197°:

0·1981 gave 0·5280 CO_2 and 0·1131 H_2O . $\text{C} = 72\cdot66$; $\text{H} = 6\cdot34$.

$\text{C}_{26}\text{H}_{27}\text{O}_3\text{N}_3$ requires $\text{C} = 72\cdot7$; $\text{H} = 6\cdot3$ per cent.

Both these compounds are insoluble in benzene or dry ether.

Normal Ethyl β -Methylglutaconate, $\text{CO}_2\text{H} \cdot \dot{\text{C}}\text{H} \cdot \text{CHMe} \cdot \dot{\text{C}}\text{H} \cdot \text{CO}_2\text{H}$. —The ethyl ester of this acid has been prepared by Genvresse (*Ann. Chim. Phys.*, 1891, [vi], **24**, 119) and by Feist (*Annalen*, 1906, **345**, 89), but it was obtained in both cases by the esterification of the crude mixture of the two modifications. We have therefore prepared this substance from the pure normal acid melting at 147°, by esterifying it with alcohol and sulphuric acid in the usual manner. It boils at 165°/70 mm. as a clear, mobile oil:

0·1872 gave 0·4112 CO_2 and 0·1362 H_2O . $\text{C} = 59\cdot91$; $\text{H} = 8\cdot08$.

$\text{C}_{10}\text{H}_{16}\text{O}_4$ requires $\text{C} = 60\cdot0$; $\text{H} = 8\cdot0$ per cent.

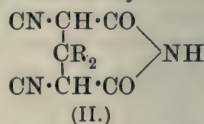
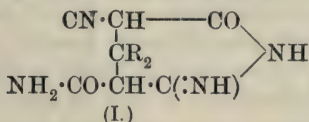
This ester was treated with ethyl sodiocyanoacetate in precisely the same manner as the labile ester, and although a small amount of a substance of high boiling point was isolated, no definite fraction could be obtained. The fraction boiling at 210—215°/20 mm. (about 2 grams from 42 grams of the ester) was hydrolysed, but no trace of $\beta\beta$ -dimethylpropanetricarboxylic acid could be isolated.

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CLXXIII.—*The Formation and Reactions of Imino-compounds. Part XVIII. The Condensation of cycloHexanones with Cyanoacetamide Involving the Displacement of an Alkyl Group.*

By JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD.

DURING the course of the experiments described in Part XV of this series (T., 1911, **99**, 422), which dealt with the products formed by the condensation of ketones with cyanoacetamide in the presence of piperidine, it was shown that whereas the chief product is the cyclic imino-compound I, a second substance is always formed in small amount, which can be distinguished from the imino-compound by being soluble in dilute alkali. Considerable quantities of this by-product having accumulated, we have been enabled to establish its structure, although considerable difficulty was experienced in obtaining concordant results on analysis. Ultimately this trouble was overcome by mixing the substance in the boat with powdered lead chromate and using the modified form of the Dennstedt furnace which is in vogue in the laboratories at Manchester. There can be no question that the by-products which are produced from acetone, methyl ethyl ketone, and *cyclo*-hexanone are identical with the compounds obtained as the main products by Guareschi and his collaborators in the interaction of the ketones and ethyl cyanoacetate in the presence of alcoholic ammonia, and which have a structure represented by formula II:



A comparison of the melting points of these compounds indicated their identity:

By-product from	M. p.	From ethyl cyanoacetate.
Acetone	212°	216—217°*
Methyl ethyl ketone.....	192	192—193†
<i>cyclo</i> Hexanone	207	210—211‡

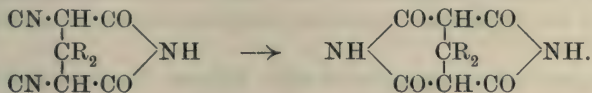
* Guareschi and Grande, *Chem. Centr.*, 1899, **2**, 439.

† Grande, *ibid.*, 1897, **1**, 903.

‡ Guareschi, *Atti. R. Accad. Sci. Torino*, 1911, **46**, 662; Squintani, *ibid.* 1912-13, **48**, 675.

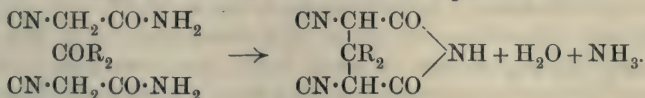
Their structure is, however, placed beyond doubt by the fact that when treated with concentrated sulphuric acid they are con-

verted into the di-imides of the tetracarboxylic acids in accordance with the scheme:



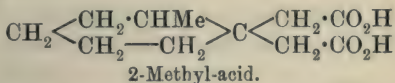
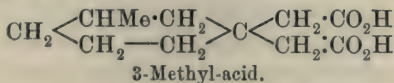
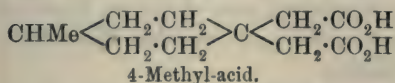
These di-imides are well-defined substances, and a comparison with the same compounds prepared by methods already described (T., 1911, 99, 436, 442, 448) showed them to be identical.

It is evident, therefore, that in the condensation of cyanoacetamide with ketones through the agency of piperidine, a small proportion reacts in accordance with the equation:



the product being present in the form of an ammonium salt, as described by Guareschi, which is decomposed by acids. It was found, moreover, that the amount of this by-product is considerably increased if the condensation is allowed to take place at a higher temperature.

In Part XV (*loc. cit.*) it was shown that *cyclohexane-1:1*-diacetic acid can be prepared by the hydrolysis of the condensation product formed from cyanoacetamide and *cyclohexanone*. Primarily with the object of preparing the methyl acids for the purposes of resolution, experiments which are now in progress, we have condensed the three methyl*cyclohexanones* with cyanoacetamide in the hope of isolating the three acids:



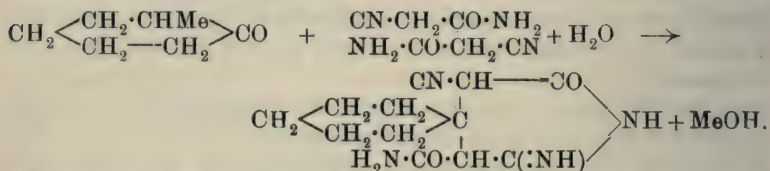
So far as the formation of the 4- and 3-methyl-acids is concerned, the reaction proceeds in precisely the same manner as with *cyclohexanone*, and the amounts formed are about the same.

On the other hand, the condensation between 2-methyl*cyclohexanone* and cyanoacetamide proceeds very slowly, and a yield of scarcely 15 per cent. of an imino-base is obtainable after several days. The examination and hydrolysis of this product proved it to be the same as that derived from *cyclohexanone*, and we there-

fore naturally concluded that the 2-methylcyclohexanone used contained some cyclohexanone, and that the presence of the methyl group in the 2-position inhibited the formation of a condensation product.

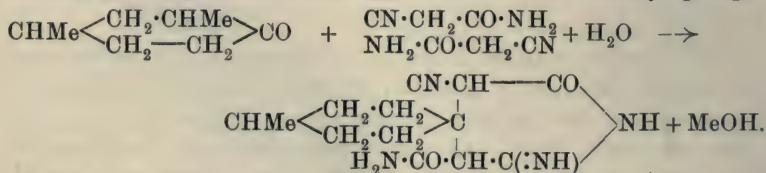
We therefore communicated with Messrs. Poulenc Frères, who were kind enough to send us a specimen of pure 2-methylcyclohexanone free from any trace of cyclohexanone, but this substance was found to react in precisely the same manner with cyanoacetamide. The ketone certainly appeared to be quite pure; it boiled at the right temperature, and yielded the characteristic semicarbazone, which, without purification, melted at 191—192°* (the semicarbazone of cyclohexanone melts at 163°).

We were therefore forced to the conclusion that the great tendency for the ketone to react with cyanoacetamide, and the inability of the 2-methyl derivative to form a condensation product, had led to the displacement of the methyl group, probably in accordance with the scheme:



In order to obtain further evidence on this matter, we obtained some pure 2:4-dimethylcyclohexanone, which, as Messrs. Poulenc Frères inform us, is prepared from pure *m*-4-xenol by the Sabatier-Senderens process and cannot therefore contain 4-methylcyclohexanone. The ketone was, moreover, proved to be pure by the possession of the right boiling point and by the immediate precipitation of the pure semicarbazone.

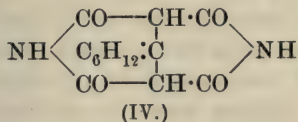
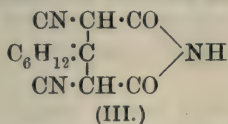
This ketone reacts with cyanoacetamide rather more rapidly than 2-methylcyclohexanone, but the product is the same as that derived from 4-methylcyclohexanone, and yields 4-methylcyclohexanone-1:1-diacetic acid on hydrolysis. It would appear, therefore, that this reaction also involves the elimination of the 2-methyl group:



In all these reactions the formation of the acid by-product was

* The condensation was also tried with a specimen which had been regenerated from the pure oxime *m. p.* 43·44°, with the same result,

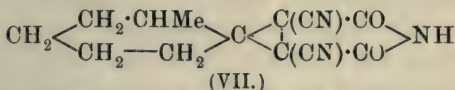
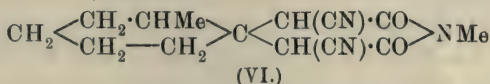
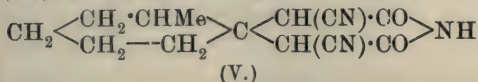
always observed, and in the cases of the 4- and 3-methylcyclohexanones they were proved to be identical with the compounds recently prepared by Squintani (*Atti. R. Accad. Sci. Torino*, 1912-13, **48**, 675) by the action of ethyl cyanoacetate on the methylcyclohexanone in the presence of alcoholic ammonia, and which have the formula III:



The melting point of the 4-methyl compound (215°) is comparable with the melting point 210—211° found by him. The 3-methyl derivative, melting at 240°, compares with the melting point 240—241° found by Guareschi (*loc. cit.*, **46**, 662). The structure of these by-products is, however, apparent from the formation of the di-imides (4) in the manner already described.

The by-product from 2-methylcyclohexanone and from 2:4-dimethylcyclohexanone are the same as from cyclohexanone and from 4-methylcyclohexanone respectively.

Squintani also describes the preparation of a condensation product from 2-methylcyclohexanone and ethyl cyanoacetate in the presence of alcoholic ammonia, which melts at 210°, and to which he gives the formula V. He has also prepared the methyl imide (VI) and a *spiro*-compound of formula VII:



An examination of the melting points given for these substances, compared with those of the similar compounds derived from cyclohexanone, does not reveal any marked differences:

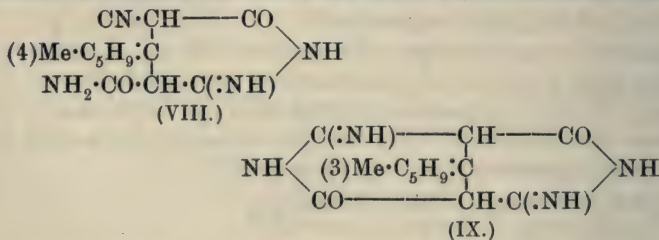
	2-Methylcyclo- hexanone.	cyclo- Hexanone.
Imide (V.)	†210°	*211—212°
Methylimide (VI.)	†181—182°	†175°
<i>spiro</i> -Compound (VII.)	†235—236	*238—240
	* Guareschi. † Squintani.	

There is a difference of about 1·5 per cent. on the carbon content and of about 1 per cent. on the nitrogen content of these substances, but, as we have already mentioned, it is a matter of some difficulty

to obtain concordant results from these compounds on combustion,* and it is possible that Squintani's 2-methyl compounds may be the same as those derived from *cyclohexanone*. It would be of interest, therefore, to know whether his substances are converted into the easily characterised *cyclohexane*-1:1-diacetic acid on hydrolysis, or whether they yield the unknown 2-methyl acid. In our hands, the reaction described by Squintani led to derivatives of *cyclohexanone* only, but we were unable to obtain more than a few grams of the condensation product.

It is evident that the elimination of a methyl group in this manner requires to be further investigated, and experiments with this object in view are now in progress.

During the course of the experiments described in this communication a remarkable difference was noticed in the behaviour of 4-methyl*cyclohexanone* and 3-methyl*cyclohexanone* in condensation with cyanoacetamide, for whereas the former yields the normal product of formula VIII, the latter yields the double ring compound of formula IX under the same experimental conditions:



The two types can be readily distinguished, because the compound of formula VIII forms a platinichloride containing two equivalents of the base, whereas the platinichloride of formula IX contains one equivalent only. It is probable that this difference is due to the length of time required for the base to start precipitating from the solution, and is not influenced by any tendency for the position of the methyl group to cause the formation of the second ring. This can be demonstrated by experiment, because, if the condensation of 4-methyl*cyclohexanone* with cyanoacetamide is carried out in a solution sufficiently dilute to prevent precipitation of the base until eight to nine hours have elapsed, it is the di-imino-di-imide corresponding with formula IX that is precipitated.

Again, in the reactions between 2-methyl*cyclohexanone* and cyanoacetamide, and 2:4-dimethyl*cyclohexanone* and cyanoacetamide, which lead to derivatives of *cyclohexane* and 4-methyl*cyclo-*

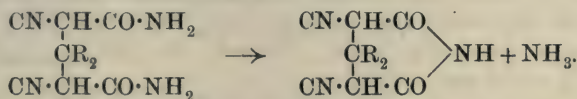
* Actually, Mr. F. B. Thole carried out twelve combustions of one of these compounds, and one of us (A. S. W.) has performed nine of another without obtaining two concordant results.

hexane respectively, and in which several hours have to elapse before the condensation bases commence to be precipitated, it is the di-imino-base that is formed in each case.

The following table shows the melting points of the compounds obtained compared with those from *cyclohexanone*:

	Imino- base.	Di-imino- base.	Mono- imide.	Di- imide.	Dicyano- imide.	Acid.	An- hydride.	Anthic acid.	Imide.
<i>cyclo</i> - Hexane	305°	303°	260°	400—405°	207°	181°	73°	146°	168°
4-Methyl- <i>cyclo</i> - hexane	284	279	225	324—325	215	158	53	184	162
3-Methyl- <i>cyclo</i> - hexane	—	268	—	310	240	143	19	172	155

In all these condensations it was noticed that the precipitation of the bases ceased after about seventy-two hours. An examination of the liquid revealed the presence of free ammonia, formed evidently in the production of the by-product, or by the dissociation of its ammonium salt:



It followed, therefore, that ammonia exerted an inhibiting effect on the formation of the condensation product, and this was proved to be the case by the addition of a small quantity of this substance to the original condensation mixture when no precipitation of the base ensued.

This fact is of importance, because it was found that unless cyanoacetamide is freed from the last traces of the ammonia used in its preparation, no condensation bases could be formed from it. This purification cannot be effected by washing, and it is always necessary to heat the amide at 100° for some hours prior to use.

EXPERIMENTAL.

The Structure of the By-products formed from Ketones and Cyanoacetamide in the presence of Piperidine.

The by-products occur as ammonium salts, and remain in the solution after the piperidone base (T., 1911, **99**, 430) has been separated. The ammonium salts will crystallise from the solution on long keeping, but the free acid is readily precipitated on the addition of dilute hydrochloric acid.

Acetone.—The compound crystallises from alcohol in small needles, which melt at 212°. (Found, C=56·47; H=4·76. C₉H₉O₂N₃ requires C=56·6; H=4·7 per cent.) The structure of

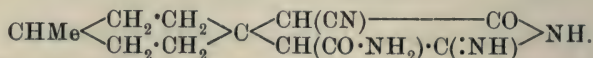
this substance as 3:5-dicyano-2:6-diketo-4:4-dimethylpiperidine, $\text{CMe}_2 \left\langle \begin{smallmatrix} \text{CH}(\text{CN}) \cdot \text{CO} \\ \text{CH}(\text{CN}) \cdot \text{CO} \end{smallmatrix} \right\rangle \text{NH}$, was proved by its complete hydrolysis to $\beta\beta$ -dimethylglutaric acid by means of 80 per cent. sulphuric acid, and by the formation of the di-imide (*loc. cit.*, p. 436). The last-named substance is formed when the piperidine derivative, dissolved in ten times its weight of concentrated sulphuric acid, is allowed to remain for twenty-four hours; when the acid is poured into twice its volume of water a clear solution is formed, from which the di-imide slowly crystallises. (Found, $\text{N}=13.43$. $\text{C}_9\text{H}_{10}\text{O}_4\text{N}_2$ requires $\text{N}=13.3$ per cent.)

Methyl Ethyl Ketone.—3:5-Dicyano-2:6-diketo-4-methyl-4-ethylpiperidine, $\text{CMeEt} \left\langle \begin{smallmatrix} \text{CH}(\text{CN}) \cdot \text{CO} \\ \text{CH}(\text{CN}) \cdot \text{CO} \end{smallmatrix} \right\rangle \text{NH}$, crystallises from alcohol in small, colourless prisms, which melt at 192° . (Found, $\text{C}=58.39$; $\text{H}=5.44$. $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}_3$ requires $\text{C}=58.5$; $\text{H}=5.4$ per cent.) The compound is converted into β -methyl- β -ethylglutaric acid on hydrolysis with 80 per cent. sulphuric acid, and yields the di-imide, melting at $330\text{--}331^\circ$ (*loc. cit.*, p. 442), when treated with cold concentrated sulphuric acid. (Found, $\text{N}=12.65$. $\text{C}_{10}\text{H}_{12}\text{O}_4\text{N}_2$ requires $\text{N}=12.5$ per cent.)

cycloHexanone.—The ω -imide of $\alpha\alpha'$ -dicyanocyclohexane-1:1-diacetic acid, $\text{CH}_2 \left\langle \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \right\rangle \text{C} \left\langle \begin{smallmatrix} \text{CH}(\text{CN}) \cdot \text{CO} \\ \text{CH}(\text{CN}) \cdot \text{CO} \end{smallmatrix} \right\rangle \text{NH}$, forms small, colourless needles from alcohol, which melt at 207° . (Found, $\text{C}=62.17$; $\text{H}=5.68$. $\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}_3$ requires $\text{C}=62.3$; $\text{H}=5.6$ per cent.) The compound is converted into cyclohexane-1:1-diacetic acid on hydrolysis with 80 per cent. sulphuric acid, and yields the di-imide, melting at $400\text{--}405^\circ$ (*loc. cit.*, p. 448), with concentrated sulphuric acid. (Found, $\text{N}=11.37$. $\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}_2$ requires $\text{N}=11.2$ per cent.)

Condensation of 4-Methylcyclohexanone with Cyanoacetamide.

The ω -Imino-imide of α -Cyano- α' -carbamyl-4-methylcyclohexane-1:1-diacetic Acid,



This substance slowly separates when a dilute alcoholic solution of 74 grams of cyanoacetamide and 50 grams of the ketone is mixed with 1 c.c. of piperidine and kept at 25° . The reaction is finished at the end of twenty-four hours, and the base (weight, 85 grams) was isolated and purified in the manner described for the similar substance from cyclohexanone (*loc. cit.*, p. 443). The

base is a colourless, micro-crystalline powder, and melts at 284° , evolving gas at a few degrees higher:

0.1872 gave 0.4075 CO_2 and 0.1174 H_2O . $\text{C}=59.36$; $\text{H}=6.97$.

$\text{C}_{13}\text{H}_{18}\text{O}_2\text{N}_4$ requires $\text{C}=59.5$; $\text{H}=6.9$ per cent.

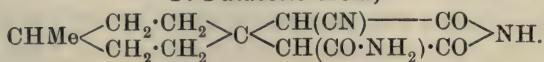
It is completely soluble in dilute hydrochloric acid, and dissolves in aqueous sodium hydroxide, forming a yellow solution.

The *platinichloride* is a yellow powder:

0.3176 gave 0.658 Pt. $\text{Pt}=20.71$.

$(\text{C}_{13}\text{H}_{18}\text{O}_2\text{N}_4)_2\text{H}_2\text{PtCl}_6$ requires $\text{Pt}=20.87$ per cent.

The ω -Imide of α -Cyano- α' -carbamyl-4-methylcyclohexane-1:1-diacetic Acid,



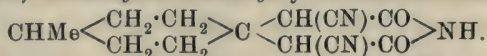
This compound is precipitated when 10 grams of the base are dissolved in dilute hydrochloric acid and the solution raised to the boiling point. It crystallises from alcohol in small, colourless prisms, which melt at 225° , and sublime, without melting, when slowly heated:

0.1903 gave 0.4130 CO_2 and 0.1128 H_2O . $\text{C}=59.20$; $\text{H}=6.59$.

$\text{C}_{13}\text{H}_{17}\text{O}_3\text{N}_3$ requires $\text{C}=59.3$; $\text{H}=6.5$ per cent.

The imide is soluble in dilute aqueous sodium carbonate.

The ω -Imide of $\alpha\alpha'$ -Dicyano-4-methylcyclohexane-1:1-diacetic Acid,



This substance occurs to the extent of about 10 per cent. in the original condensation, and can be isolated by acidifying the mother liquors after the separation of the base. It crystallises from alcohol in small, colourless needles, which melt at 215° :

0.1363 gave 0.3176 CO_2 and 0.0769 H_2O . $\text{C}=63.54$; $\text{H}=6.20$.

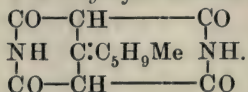
$\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}_3$ requires $\text{C}=63.7$; $\text{H}=6.1$ per cent.

The compound is characterised by the formation of a sparingly soluble *sodium* salt, which separates from a solution of the acid in aqueous sodium hydrogen carbonate. It crystallises from water in colourless needles:

0.3084 gave 0.0735 Na_2SO_4 . $\text{Na}=7.92$.

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_3\text{Na}$, H_2O requires $\text{Na}=8.0$ per cent.

The dicyano-derivative is converted into the di-imide (see next paragraph) by concentrated sulphuric acid, and is hydrolysed by boiling 80 per cent. sulphuric acid to 4-methylcyclohexane-1:1-diacetic acid.

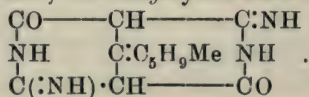
The Di-imide of 4-Methylcyclohexane-1:1-dimalonic Acid,

This substance is formed by the action of cold concentrated sulphuric acid on any one of the three compounds mentioned above, by allowing a solution in ten times its weight of concentrated acid to remain for twenty-four hours, and can be isolated by pouring the acid on to ice. The substance is dimorphous, and separates from glacial acetic acid in small needles, which slowly change to well-defined prisms, melting at 324—325°:

0.1842 gave 0.3980 CO₂ and 0.1020 H₂O. C=58.92; H=6.15.

C₁₃H₁₆O₄N₂ requires C=59.1; H=6.1 per cent.

The di-imide is soluble in aqueous sodium carbonate, but is very sparingly soluble in all the usual organic solvents excepting hot glacial acetic acid.

The Di-imino-di-imide of 4-Methylcyclohexane-1:1-dimalonic Acid,

In the condensation between 4-methylcyclohexanone and cyanoacetamide described on p. 1593, as in all these condensations, just enough water and alcohol were used to ensure complete solution. In the present experiment this solution was diluted to half its volume with dilute alcohol, and was then kept at 25°. No precipitation of the base was apparent until after twelve hours, when the separation was very rapid, and was complete after twenty-four hours. The product, purified in the usual way, is a white, crystalline powder, which melts at 279°:

0.1910 gave 0.4157 CO₂ and 0.1197 H₂O. C=59.36; H=6.97.

C₁₃H₁₈O₂N₄ requires C=59.5; H=6.9 per cent.

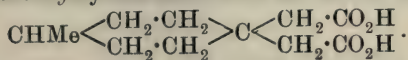
The compound is sparingly soluble in all solvents; it dissolves in aqueous alkali hydroxide, forming a colourless solution, and with hot dilute hydrochloric acid is at once transformed into the di-imide.

The *platinichloride* is a yellow powder:

0.2968 gave 0.0857 Pt. Pt=28.84.

C₁₃H₁₈O₂N₄·H₂PtCl₆ requires Pt=29.01 per cent.

4-Methylcyclohexane-1:1-diacetic Acid,



This acid is formed by the action of concentrated sulphuric acid of any one of the compounds described above under conditions which are fully described in the case of the lower homologue (*loc. cit.*, p. 445). It separates from water, or, better, from water containing a little alcohol, in long, flattened needles, which melt at 158°:

0.2023 gave 0.4578 CO₂ and 0.1520 H₂O. C=61.72; H=8.35.

C₁₁H₁₈O₄ requires C=61.7; H=8.4 per cent.

The acid is more soluble in benzene than cyclohexane-1:1-diacetic acid.

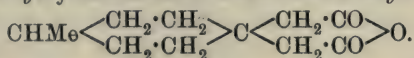
The *silver* salt is a white, crystalline precipitate:

0.3162 gave 0.1592 Ag. Ag=50.34.

C₁₁H₁₆O₄Ag₂ requires Ag=50.46 per cent.

The copper and lead salts are insoluble; the properties of the barium and calcium salts are given in the table on p. 1598.

4-Methylcyclohexane-1:1-diacetic Anhydride,



The acid readily reacts with acetyl chloride at the temperature of the boiling reagent, and the anhydride can be isolated by distillation. It boils at 212°/20 mm., and the distillate sets to a solid mass on cooling. When recrystallised from light petroleum, it forms large, transparent laminae, which melt at 53°:

0.1861 gave 0.4599 CO₂ and 0.1369 H₂O. C=67.41; H=8.18.

C₁₁H₁₆O₃ requires C=67.4; H=8.2 per cent.

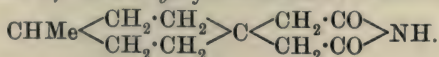
When boiled with water, the anhydride is converted into the acid from which it was derived.

The *anilic acid*, prepared from the anhydride and aniline in benzene solution, crystallises from methyl alcohol in large, colourless needles, which melt at 184°:

0.2038 gave 0.5244 CO₂ and 0.1464 H₂O. C=70.17; H=7.98.

C₁₇H₂₃O₃N requires C=70.6; H=8.0 per cent.

The Imide of 4-Methylcyclohexane-1:1-diacetic Acid,



This compound occurs as a by-product in the preparation of the acid, and can be isolated from the ethereal mother liquors after

the acid has been extracted by aqueous sodium carbonate. It crystallises from ether in small, colourless prisms, which melt at 162° :

0.1858 gave 0.4600 CO_2 and 0.1472 H_2O . $\text{C}=67.53$; $\text{H}=8.81$.

$\text{C}_{11}\text{H}_{17}\text{O}_2\text{N}$ requires $\text{C}=67.7$; $\text{H}=8.7$ per cent.

The imide is soluble in benzene and in alcohol.

The *silver* salt, prepared by the addition of aqueous silver nitrate to a solution of the imide in excess of aqueous ammonia, is a white, crystalline powder:

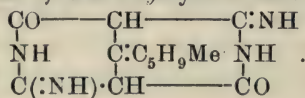
0.3179 gave 0.1132 Ag. $\text{Ag}=35.61$

$\text{C}_{11}\text{H}_{16}\text{O}_2\text{NAg}$ requires $\text{Ag}=35.76$ per cent.

The imide is readily hydrolysed to the acid by concentrated sulphuric acid.

Condensation of 3-Methylcyclohexanone with Cyanoacetamide.

The Di-imino-di-imide of 3-Methylcyclohexane-1:1-dimalonic Acid,



This substance is slowly precipitated when a dilute alcoholic solution of 74 grams of cyanoacetamide and 50 grams of 3-methylcyclohexanone with 1 c.c. of piperidine is kept at 25° , and the separation is practically complete at the end of twenty-four hours (weight, 79 grams). It is insoluble in all neutral solvents, but can be purified by solution in dilute hydrochloric acid and reprecipitation by means of aqueous sodium acetate, when it is obtained as a white, crystalline powder, which melts at 268° :

0.1837 gave 0.3999 CO_2 and 0.1154 H_2O . $\text{C}=59.38$; $\text{H}=6.98$.

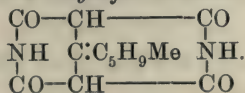
$\text{C}_{13}\text{H}_{18}\text{O}_2\text{N}_4$ requires $\text{C}=59.5$; $\text{H}=6.9$ per cent.

The di-imino-di-imide dissolves in aqueous potassium hydroxide, forming a colourless solution; its diacid character is shown by the formation of the *platinichloride*, which is a yellow powder:

0.3951 gave 0.1143 Pt. $\text{Pt}=28.93$.

$\text{C}_{13}\text{H}_{18}\text{O}_2\text{N}_4\cdot\text{H}_2\text{PtCl}_6$ requires $\text{Pt}=29.01$ per cent.

In this condensation the formation of the di-imino-di-imide appears to be complete, for we were unable to isolate any trace of the mono-acid base.

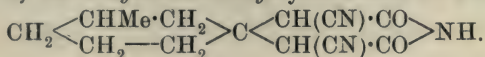
The Di-imide of 3-Methylcyclohexane-1:1-dimalonic Acid,

The compound is precipitated when a solution of the above base in dilute hydrochloric acid is raised to the boiling point. It is also formed by the action of concentrated sulphuric acid on the dicyano-derivative described below, and can be purified by recrystallisation from glacial acetic acid, from which solvent it separates in small, glistening prisms, melting at 310° :

0.1298 gave 0.2816 CO_2 and 0.0698 H_2O . $\text{C}=59.16$; $\text{H}=5.98$.

$\text{C}_{13}\text{H}_{16}\text{O}_4\text{N}_2$ requires $\text{C}=59.1$; $\text{H}=6.1$ per cent.

The di-imide is sparingly soluble in all the usual organic solvents, excepting hot glacial acetic acid. It dissolves in a warm aqueous solution of sodium carbonate.

The ω-Imide of αα'-Dicyano-3-methylcyclohexane-1:1-diacetic Acid,

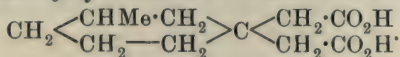
When the mother liquors, after the separation of the di-imino-base, are acidified by dilute mineral acid, this compound is precipitated (weight, 20 grams). It crystallises from alcohol in colourless needles, melting at 240° :

0.1743 gave 0.4057 CO_2 and 0.0957 H_2O . $\text{C}=63.44$; $\text{H}=6.10$.

0.1182 „ 17.8 c.c. N_2 at 19° and 746 mm. $\text{N}=16.91$.

$\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}_3$ requires $\text{C}=63.7$; $\text{H}=6.1$; $\text{N}=17.1$ per cent.

The substance is converted into the di-imide by cold concentrated sulphuric acid, and is transformed into 3-methylcyclohexane-1:1-diacetic acid when hydrolysed by 80 per cent. sulphuric acid.

3-Methylcyclohexane-1:1-diacetic Acid,

This acid is formed by the hydrolysis of the compounds described above with 80 per cent. aqueous sulphuric acid, and can be isolated in the manner already described (*loc. cit.*, p. 445). It separates from water containing a little alcohol in needle clusters, which melt at 143° :

0.1569 gave 0.3530 CO_2 and 0.1176 H_2O . $\text{C}=61.54$; $\text{H}=8.33$.

$\text{C}_{11}\text{H}_{18}\text{O}_4$ requires $\text{C}=61.7$; $\text{H}=8.4$ per cent.

The acid can also be recrystallised from benzene.

The *silver* salt is a white, crystalline powder:

0·3102 gave 0·1566 Ag. $\text{Ag} = 50·48$.

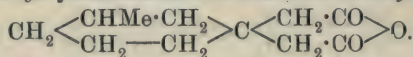
$\text{C}_{11}\text{H}_{16}\text{O}_4\text{Ag}_2$ requires $\text{Ag} = 50·46$ per cent.

The copper and lead salts are insoluble. The three acids of this series may, however, be readily distinguished by the aid of their calcium and barium salts, which are formed by the action of normal solutions of the metallic chlorides on a $N/2$ -solution of the ammonium salts of the acids. This is shown in the following table:

Salt.	<i>cyclo</i> Hexane- 1:1-diacetic acid.	3-Methyl <i>cyclo</i> hexane- 1:1-diacetic acid.	4-Methyl <i>cyclo</i> hexane- 1:1-diacetic acid.
Ba.....	Soluble.	Soluble.	Crystalline precipitate on boiling; does not dissolve on cooling.
Ca.....	Crystalline precipitate on boiling; does not dissolve on cooling.	Crystalline precipitate on boiling; redissolves on cooling.	Amorphous, insoluble precipitate in the cold.*

* No precipitate is formed in $N/5$ solution in the cold, but the salt separates in the crystalline condition on boiling.

3-Methylcyclohexane-1:1-diacetic Anhydride,



This anhydride is formed by the action of excess of acetyl chloride on the acid at the temperature of the boiling reagent, and can be isolated by distilling the product. It boils at $212^\circ/20$ mm., and the distillate sets to a solid mass of needles on being cooled to 0° . It may be obtained in long, colourless needles, melting at 19° , by cooling a solution in light petroleum to 0° :

0·1856 gave 0·4571 CO_2 and 0·1334 H_2O . $\text{C} = 67·16$; $\text{H} = 7·99$.

$\text{C}_{11}\text{H}_{16}\text{O}_3$ requires $\text{C} = 67·4$; $\text{H} = 8·2$ per cent.

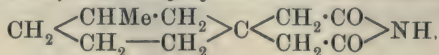
The anhydride yields the acid from which it was derived when boiled with water.

The *anilic acid*, from the anhydride and aniline in benzene solution, crystallises from dilute alcohol in colourless plates, which melt at 172° :

0·1421 gave 0·3680 CO_2 and 0·1038 H_2O . $\text{C} = 70·62$; $\text{H} = 8·12$.

$\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}$ requires $\text{C} = 70·6$; $\text{H} = 8·0$ per cent.

The Imide of 3-Methylcyclohexane-1:1-diacetic Acid,



A small quantity of this compound was formed by the incomplete hydrolysis of the di-imino-base with concentrated sulphuric acid, and was found in the ethereal solution after the acid had been

extracted by aqueous sodium carbonate. It separates from dry ether in slender, colourless needles, which melt at 155° :

0.1893 gave 0.4694 CO_2 and 0.1501 H_2O . $\text{C}=67.61$; $\text{H}=8.81$.

$\text{C}_{11}\text{H}_{17}\text{O}_2\text{N}$ requires $\text{C}=67.7$; $\text{H}=8.7$ per cent.

The imide is readily soluble in alcohol and in benzene.

Condensation of 2-Methylcyclohexanone with Cyanoacetamide.

This condensation was carried out with 74 grams of cyanoacetamide and 50 grams of the ketone dissolved in dilute alcohol and mixed with 1 c.c. of piperidine. As only a trace of precipitate had formed after remaining for twenty-four hours at 25° , the solution was left for three days, and the solid collected. It weighed 15 grams, and when purified by solution in dilute hydrochloric acid and reprecipitation by aqueous sodium acetate, it melted at 303° . (Found, $\text{N}=22.47$. $\text{C}_{12}\text{H}_{16}\text{O}_2\text{N}_4$ requires $\text{N}=22.6$, and $\text{C}_{13}\text{H}_{18}\text{O}_2\text{N}_4$ requires $\text{N}=21.3$ per cent.) Since the di-imino-di-imide and di-imide of *cyclohexane-1:1*-dimalonic acid melt so closely together, it was necessary to analyse the platinichloride in order to show that the substance in hand was the di-imino-base. (Found, $\text{Pt}=29.49$. $\text{C}_{12}\text{H}_{14}\text{O}_2\text{N}_4\cdot\text{H}_2\text{PtCl}_6$ requires $\text{Pt}=29.6$ per cent.)

The base was then converted into the di-imide by hot dilute hydrochloric acid. When recrystallised from glacial acetic acid, it melted at $400\text{--}405^{\circ}$. (Found, $\text{C}=11.39$. $\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}_2$ requires $\text{N}=11.2$, and $\text{C}_{13}\text{H}_{16}\text{O}_4\text{N}_2$ requires $\text{N}=10.6$ per cent.)

The di-imide was then hydrolysed by concentrated sulphuric acid to the non-nitrogenous acid. When recrystallised from water, it melted at 181° . (Found, $\text{C}=59.95$; $\text{H}=8.03$. $\text{C}_{10}\text{H}_{16}\text{O}_4$ requires $\text{C}=60.0$; $\text{H}=8.0$; and $\text{C}_{11}\text{H}_{18}\text{O}_4$ requires $\text{C}=61.7$; $\text{H}=8.4$ per cent.)

The anhydride of this acid melted at 73° , and the anilic acid at 146° . They were proved to be identical with the compounds derived from *cyclohexanone* both by direct comparison and by analysis.

There can therefore be no question that the compounds formed in this condensation are derivatives of *cyclohexanone*.

When the mother liquors from the condensation are acidified, a small quantity of acid by-product is precipitated. This was found to be the ω -imide of $\alpha\alpha'$ -dicyanocyclohexane-1:1-diacetic acid, melting at 207° . (Found, $\text{C}=62.19$; $\text{H}=5.72$. $\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}_3$ requires $\text{C}=62.3$; $\text{H}=5.6$ per cent.)

A similar condensation conducted with a specimen of 2-methylcyclohexanone, which had been specially purified (see p. 1588), gave the same results as those described above.

The Condensation of 2:4-Dimethylcyclohexanone with Cyanoacetamide.

In this instance 74 grams of cyanoacetamide, 60 grams of the pure ketone, and 1 c.c. of piperidine, in dilute alcoholic solution, were kept at 25°. At the end of forty-eight hours, 30 grams of solid base had separated, and this was collected and purified in the usual manner. It melted at 279°. (Found, C=59.33; H=6.94. $C_{13}H_{18}O_2N_4$ requires C=59.5; H=6.9; and $C_{14}H_{20}O_2N_4$ requires C=60.9; H=7.2 per cent.) The structure of this substance as the di-imino-di-imide was proved by the analysis of the platinichloride. (Found, Pt=28.91. $C_{13}H_{18}O_2N_4, H_2PtCl_6$ requires Pt=29.01 per cent.)

The di-imide prepared from this base and hot dilute hydrochloric acid formed well-defined prisms from glacial acetic acid, and melted at 324–325°. (Found, C=58.87; H=6.17. $C_{13}H_{16}O_4N_2$ requires C=59.1; H=6.1; and $C_{14}H_{18}O_4N_2$ requires C=60.4; H=6.5 per cent.)

The non-nitrogenous acid formed from these compounds with concentrated sulphuric acid melted at 158. (Found, C=61.73; H=8.46. $C_{11}H_{18}O_4$ requires C=61.7; H=8.4; and $C_{12}H_{20}O_4$ requires C=63.2; H=8.8 per cent.)

The acid was further identified as 4-methylcyclohexanone-1:1-diacetic acid by the formation of the anhydride melting at 53°, and of the anilic acid melting at 184°.

There can be no doubt, therefore, that the compounds formed in this condensation are derivatives of 4-methylcyclohexanone.

When the filtrate from the di-imino-base is acidified, 10 grams of the acid by-product are precipitated. This was found to be the ω -imide of $\alpha\alpha'$ -dicyano-4-methylcyclohexane-1:1-diacetic acid, melting at 215°. (Found, C=63.58; H=6.19. $C_{13}H_{15}O_2N_3$ requires C=63.7; H=6.1 per cent.)

It was noticed that in both the last-named condensations the precipitation of the base ceased after about seventy-two hours. This was found to be due to the inhibiting action of ammonia formed in the condensation (see p. 1591). The recovered ketones were found to condense with cyanoacetamide in the same manner as the pure substances.

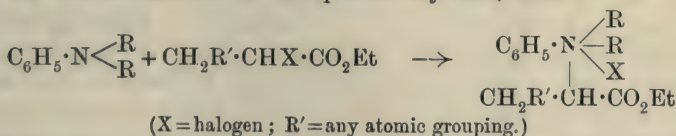
THE SORBY RESEARCH LABORATORY,
THE UNIVERSITY, SHEFFIELD.

CLXXIV.—*The Replacement of Alkyl Groups in Tertiary Aromatic Bases.*

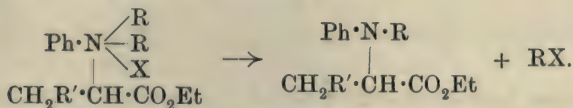
By JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD.

THE use of the dialkylanilines for the purpose of eliminating halogen hydride from halogen derivatives of fatty ethereal salts was first suggested by Weinig (*Annalen*, 1894, **280**, 253), and the method has been used by numerous investigators since that time. It is evident, however, from the experiments of Crossley and Le Sueur (T., 1899, **75**, 162) that the yield of unsaturated ester varies with the structure of the halogen ester treated, and is, in many cases, far from satisfactory.

As a matter of fact, the present authors have found this method to fail in so many cases in which success might reasonably have been expected that they have decided to place on record a series of experiments which shows the unsuitability of these bases for the purpose of eliminating halogen hydride from any substances excepting those, such as ethyl α -bromoisovalerate, in which the formation of the unsaturated ester takes place with great ease, and that even in such instances the yield of the unsaturated ester is entirely dependent on the conditions of the experiment. In the present paper it is shown that the initial reaction between a dialkylaniline and a bromo- or chloro-ethereal salt, capable of eliminating hydrogen bromide or chloride from within its molecule, involves the formation of the quaternary salt, thus:



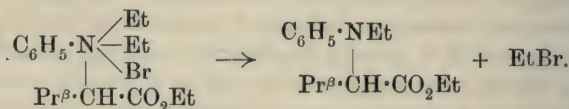
When once this salt is formed, it is impossible to eliminate hydrogen haloid from it on heating; actually under these conditions it passes into the alkyl haloid and the more highly substituted derivative of aniline, thus:



The quaternary salts are formed at the ordinary temperature, and the rate of formation is dependent on the nature of the halogen derivative used; their formation is, moreover, facilitated by the addition of a trace of some hydroxylic solvent, such as alcohol.

The so-called normal reaction between the base and the halogen derivative (involving the elimination of hydrogen haloid) is a secondary reaction which takes place at a higher temperature, and then only between that portion of the reacting mixture which, under the experimental conditions used, has not passed into the quaternary salt.

An excellent example illustrating this statement is supplied by the well-known reaction by which ethyl α -bromo*isovalerate* is converted into ethyl dimethylacrylate, to the extent of 80 per cent., by diethylaniline. Actually, this yield is only obtained if the mixture of base and halogen derivative is immediately raised to the boiling point. The formation of the quaternary salt takes place, in this case, only slowly at the ordinary temperature, but if the mixture is allowed to remain for seventy-two hours, and is then boiled, the yield of the unsaturated ester is reduced to 50 per cent., the remainder of the product being the substituted aniline formed in accordance with the equation:



In other cases, such as ethyl α -bromopropionate and ethyl α -bromo-*n*-butyrate, the tendency for the production of the quaternary salt is so considerable that even when these substances are mixed with diethylaniline and immediately raised to the boiling point, only a comparatively poor yield of the unsaturated ester is obtained, and the main product comprises the more highly substituted aniline; when the mixture is allowed to remain before heating, a diminished yield of the unsaturated ester is obtained.

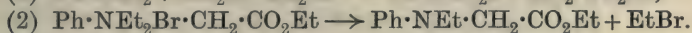
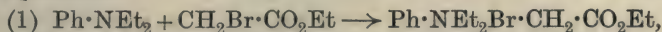
The following table shows the percentages of substituted anilines formed from bromo-etheral salts, capable of forming $\alpha\beta$ -unsaturated esters, by the action of diethylaniline:

Time.	Ethyl α -bromo- <i>isobutyrate</i> .	Ethyl α -bromo- <i>isovalerate</i> .	Ethyl α -bromo- <i>n</i> -butyrate.	Ethyl α -bromo- propionate.
Heated at once	31	20	33	90
After 24 hours	44.4	32	55	95
„ 72 „	57	45.5	68	—

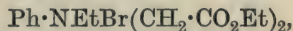
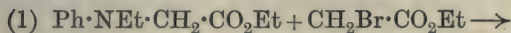
No further increase in the amount of the substituted aniline is produced after seventy-two hours, and it is therefore evident that equilibrium between the base, quaternary salt, and halogen ester is established at the end of this time in the examples investigated.

The action of diethylaniline on a bromo-ester incapable of eliminating hydrogen bromide is illustrated by the employment of

ethyl bromoacetate, for in this case the reactions represented by the equations:



are complete in the course of a few hours, and no special precautions are necessary to ensure the formation of the quaternary salt. Moreover, the further action of the bromo-ester on the above substituted aniline in accordance with the equations:

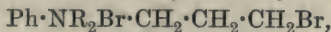


is also practically complete.

A remarkable difference between the behaviour of the three halogen derivatives of ethyl acetate towards the dialkylanilines was noticed. Thus, whereas ethyl chloroacetate reacts exceedingly slowly, and is only partly transformed into the substituted aniline after being heated for several days with diethylaniline at 180° , ethyl iodoacetate and diethylaniline are completely transformed into ethyl iodide and the substituted aniline in the course of thirty minutes at the same temperature. Ethyl bromoacetate is completely transformed into the substituted aniline after two and a-half hours under the same experimental conditions.

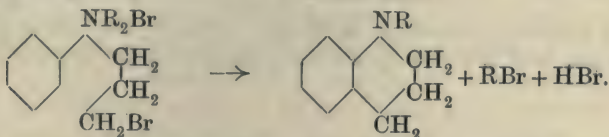
There is no essential difference between the behaviour of dimethylaniline and diethylaniline in respect of the reactions already cited, although it was noticed that the dimethyl base passed into the quaternary salt with greater rapidity than the higher alkylated aniline.

The replacement of alkyl groups in the two bases under discussion is further illustrated by their reaction with certain dihalogen derivatives of the hydrocarbons, such as trimethylene bromide and ethylene dibromide. Thus, with a dialkylaniline and trimethylene bromide, the formation of the quaternary salt:



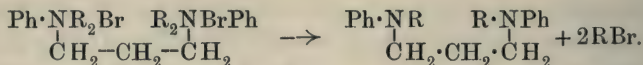
takes place very rapidly. The reaction then follows two courses, namely:

(1) Alkyl bromide and hydrogen bromide are eliminated, and *N*-alkyltetrahydroquinoline is formed, thus:



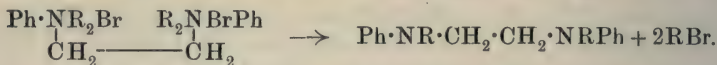
(2) A second quaternary salt is formed, and alkyl bromide alone

is evolved. The product is then diphenyldialkyltrimethylene-diamine:

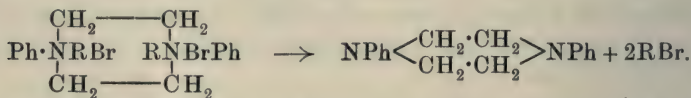


Here again the relative proportion of the two products depends entirely on the conditions of the experiment. If the mixture is immediately heated, the chief product is the quinoline derivative. If the formation of the double quaternary salt is induced to take place by allowing the reacting mixture to remain for some hours prior to being heated, the chief product is the substituted aniline. It is interesting to note that no trace of alkylallylaniline, $\text{Ph} \cdot \text{NR} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2$, is formed under any of the experimental conditions tried.

In the same way the action of ethylene dibromide on a dialkylaniline does not yield any alkylvinylaniline, but leads to the formation of the double quaternary salt, which then eliminates alkyl bromide and passes into a diphenyldialkylethylenediamine:

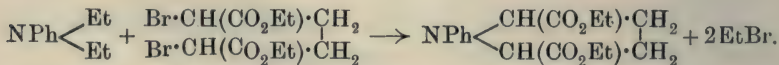


The further action of ethylene dibromide on the diphenyldialkylethylenediamine leads to the formation of another quaternary salt, which, when heated, passes into 1:4-diphenylpiperazine and the alkyl bromide, thus:



A small amount of this substance can also be isolated from the products of the initial reaction.

The formation of a ring in this manner is analogous to the production of ethyl 1-phenylpyrrolidine-2:5-dicarboxylate by the action of diethylaniline on ethyl $\alpha\delta$ -dibromoadipate (Le Sueur, T., 1909, **95**, 276; Le Sueur and Haas, *ibid.*, 1910, **97**, 173), which is represented thus:



It is probable, however, that this reaction also takes place in two stages, and that the open-chain substituted aniline is the initial product

EXPERIMENTAL.

(1) *The Action of Dialkylanilines on Bromo-esters capable of eliminating Hydrogen Bromide.*

Diethylaniline and Ethyl α -Bromopropionate.—A similar apparatus was employed in all the experiments described in this communication, and was so arranged that the amount of ethyl bromide, where diethylaniline was used, could be collected and weighed. In those cases in which dimethylaniline was employed, the amount of alkyl bromide formed was determined from the loss in weight of the containing flask. The apparatus comprised a flask, placed in an oil-bath, to which was attached an air condenser bent 30 cm. from the flask neck at an angle of 130° , and again 40 cm. beyond this bend at an angle of 50° . The further end of the condenser then passed into a Davis condenser, which communicated with a receiver cooled in ice.

When 75 grams of diethylaniline and 91 grams of ethyl α -bromopropionate are mixed and immediately raised to the boiling point, a short time elapses before the elimination of ethyl bromide commences. When once started, the reaction proceeds rapidly, and at the end of three hours 45 grams of ethyl bromide had been collected. The products were isolated by adding dilute aqueous sodium hydroxide to the contents of the flask and extracting the oil with ether. Fractionation under diminished pressure yielded a small quantity of unaltered diethylaniline and an amount of ethyl α -phenylethylaminopropionate, $\text{NEtPh}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, corresponding with a yield of 90 per cent. The base is a pale yellow oil, which boils at $156^\circ/20$ mm. (Found, $\text{C}=70.47$; $\text{H}=8.69$. $\text{C}_{13}\text{H}_{19}\text{O}_2\text{N}$ requires $\text{C}=70.6$; $\text{H}=8.6$ per cent.).

It was found that if the mixture of diethylaniline, and ethyl bromopropionate is allowed to remain for twenty-four hours previous to being heated, a slightly increased yield (up to 95 per cent.) of ethyl α -phenylethylaminopropionate can be obtained.

*Diethylaniline and Ethyl α -Bromo-*n*-butyrate.*—In this case three quantities of 97 grams of ethyl α -bromo-*n*-butyrate and 75 grams of diethylaniline were treated separately:

(a) The mixture was heated immediately to 190° and the reaction allowed to proceed. After 6.5 hours 18 grams of ethyl bromide had been collected, representing a yield of 33 per cent. of ethyl α -phenylethylamino-*n*-butyrate, $\text{NEtPh}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$.

(b) The mixture was allowed to remain for twenty-four hours, and was then heated to 190° . In this instance 30 grams of ethyl bromide were collected, representing a yield of 55 per cent. of ethyl α -phenylethylamino-*n*-butyrate.

(c) Seventy-two hours were allowed to elapse before the mixture was heated, when 37 grams of ethyl bromide were collected, corresponding with a yield of 68 per cent. of ethyl α -phenylethylamino-*n*-butyrate.

Ethyl α -phenylethylamino-*n*-butyrate is a pale yellow oil, which boils at $162^{\circ}/20$ mm. (Found, C=71.42; H=8.93. $C_{14}H_{21}O_2N$ requires C=71.5; H=8.9 per cent.)

Diethylaniline and Ethyl α -Bromoisobutyrate.—The quantities used were the same as with the normal ester, three experiments being carried out as described above. (a) Directly heated, yielded 17 grams of ethyl bromide corresponding with 31 per cent. of ethyl α -phenylethylaminoisobutyrate, $NEtPh \cdot CMe_2 \cdot CO_2Et$. (b) After twenty-four hours, gave 24 grams of ethyl bromide, representing 44.4 per cent. of the substituted aniline. (c) After seventy-two hours gave 31 grams of ethyl bromide, that is, 57 per cent. of the substituted aniline.

Ethyl α -phenylethylaminoisobutyrate boils at $163^{\circ}/20$ mm. (Found, C=71.49; H=8.97. $C_{14}H_{21}O_2N$ requires C=71.5; H=8.9 per cent.) Its isolation presents some difficulty owing to the fact that the ethyl methylacrylate formed by the elimination of hydrogen bromide from the bromo-ester polymerises under the experimental conditions used. The base can however, be extracted by 20 per cent. aqueous hydrochloric acid.

Diethylaniline and Ethyl α -Bromoisovalerate.—A mixture of 96 grams of ethyl α -bromoisovalerate and 75 grams of diethylaniline was treated in the manner already described. (a) gave 11 grams of ethyl bromide or 20 per cent. of ethyl phenylethylaminoisovalerate, $NEtPh \cdot CHPr \cdot CO_2Et$. (b) yielded 17 grams of ethyl bromide, representing 32 per cent. of the substituted aniline. (c) gave 23 grams of ethyl bromide, corresponding with 45.5 per cent. of the aniline ester.

Ethyl α -phenylethylaminoisovalerate boils at $169^{\circ}/20$ mm. (Found, C=72.21; H=9.29. $C_{15}H_{23}O_2N$ requires C=72.3; H=9.2 per cent.) The four bromo-esters mentioned above were also heated with dimethylaniline under the same experimental conditions. The yield of methyl bromide and of the substituted aniline was in every case practically the same as with diethylaniline.

(2) *The Action of Dialkylanilines on Esters incapable of Eliminating Hydrogen Bromide.*

Diethylaniline and Ethyl Bromoacetate.—The reaction between these substances is practically quantitative under the following conditions. A mixture of 167 grams of ethyl bromoacetate and

149 grams of diethylaniline is heated at 180° in an oil-bath, and the ethyl bromide collected in the manner already described. At the end of two and a-half hours, 92 grams of ethyl bromide had been obtained, and the cooled product was treated with dilute alkali and extracted.

Ethyl phenylethylaminoacetate (*phenylethylglycine ester*), $\text{NEtPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which is the only isolable substance present, is a colourless, mobile liquid, boiling at $178^{\circ}/42$ mm. and at $280^{\circ}/759$ mm.:

0.2294 gave 0.5853 CO_2 and 0.1703 H_2O . $\text{C}=69.60$; $\text{H}=8.25$.

$\text{C}_{12}\text{H}_{17}\text{O}_2\text{N}$ requires $\text{C}=69.6$; $\text{H}=8.2$ per cent.

The ester rapidly becomes brown on exposure to light and air.

The *platinichloride* is an orange-yellow, crystalline powder, which becomes almost white at 135 — 140° , and melts and decomposes at 150° :

0.2826 gave 0.0673 Pt. $\text{Pt}=23.81$.

$(\text{C}_{12}\text{H}_{17}\text{O}_2\text{N})_2, \text{H}_2\text{PtCl}_6$ requires $\text{Pt}=23.7$ per cent.

Ethyl anilinodiacetate, $\text{NPh}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, is formed in a yield of about 80 per cent. when 21 grams of ethyl phenylethylaminoacetate are heated with 20 grams of ethyl bromoacetate for eight hours; 9 grams of ethyl bromide were collected during the experiment. The ester boils at $201^{\circ}/15$ mm.:

0.1637 gave 0.3788 CO_2 and 0.1047 H_2O . $\text{C}=63.10$; $\text{H}=7.11$.

$\text{C}_{14}\text{H}_{19}\text{O}_4\text{N}$ requires $\text{C}=63.4$; $\text{H}=7.2$ per cent.

Dimethylaniline and Ethyl Bromoacetate.—There is no essential difference in the speed of the reaction between these substances and that of diethylaniline with ethyl bromoacetate, phenylmethylaninoacetate being obtained in yield of about 95 per cent. The boiling point, 156 — $157^{\circ}/17$ mm., was found for this substance, which is the same temperature as that obtained by H. Gault (*Chem. Centr.*, 1908, i, 1677).

Diethylaniline and Ethyl Chloroacetate.—The reaction between molecular quantities of these substances proceeds very slowly at the temperature of the boiling mixture, and is not complete after three days.

Diethylaniline and Ethyl Iodoacetate.—When molecular quantities of these compounds are heated at 130° , a vigorous reaction ensues, and practically the theoretical amount of ethyl iodide can be collected in the course of twenty minutes. The residue was found to consist almost entirely of ethyl phenylaminoacetate.

(3) *The Action of Dialkylanilines on Ethylene Dibromide and on Trimethylene Bromide.*

Diethylaniline and Ethylene Dibromide.—In carrying out this reaction, it was found necessary to use large quantities of material, and a mixture of 282 grams of ethylene dibromide with 450 grams of diethylaniline was heated at 180°. The evolution of ethyl bromide did not commence until the heating had been in progress for four to five hours, but after this time a rapid stream passed into the condenser, and the reaction was finished at the end of eleven hours.

Diphenyldiethylethylenediamine, $\text{NEtPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NEtPh}$, is the chief product of this reaction, and can be isolated by distillation. It boils at 245°/45 mm., and forms prisms from alcohol, which melt at 75°. (Found, C=80·85; H=9·06; N=10·64. $\text{C}_{18}\text{H}_{24}\text{N}_2$ requires C=80·6; H=9·0; N=10·5 per cent.) (compare Fröhlich, *Ber.*, 1907, **40**, 764; Wedekind and Mayer, *ibid.*, 1909, **42**, 308).

The *picrate*, which separates as a yellow, crystalline powder when alcoholic solutions of the base and picric acid are mixed, melts and decomposes at 190°. The *monopicrate* has been prepared by Fröhlich (*loc. cit.*); it melts at the same temperature. From the following analyses, there can be no doubt that our substance is the *dipicrate*:

0·1656 gave 0·3021 CO_2 and 0·0619 H_2O . C=49·74; H=4·15.

0·1151 „ 15·6 c.c. N_2 at 14° and 739 mm. N=15·42.

$\text{C}_{18}\text{H}_{24}\text{N}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ requires C=57·9; H=5·4; N=14·1 per cent.

$\text{C}_{18}\text{H}_{24}\text{N}_2 \cdot 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ „ C=49·6; H=4·1; N=15·4 „

Diphenylpiperazine, $\text{NPh} \left\langle \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \right\rangle \text{NPh}$.—This substance occurs in small amount in the product of the experiment described above, and can be isolated from the distillation residue on treatment with dry ether, in which solvent it is very sparingly soluble. Its mode of formation is evident from the fact that when diphenyldiethylethylenediamine is heated with a molecular quantity of ethylene dibromide at 190°, ethyl bromide is evolved, and in the course of eight hours a 75 per cent. yield of diphenylpiperazine is produced. The base can be isolated from the reaction mixture by adding an equal volume of dry ether, when practically the whole amount separates in a crystalline condition.

The compound crystallises from ether in silvery, white plates, which melts at 163—164°. It was proved to be identical with the diphenylpiperazine prepared by Hofmann (*Proc. Roy. Soc.*, 1859, **9**, 388; compare also Dunlop and Jones, *T.*, 1909, **95**, 419) by direct comparison with a specimen of this substance prepared from

aniline and ethylene dibromide. (Found, $C=80.78$; $H=7.60$; $N=12.05$. $C_{16}H_{18}N_2$ requires $C=80.7$; $H=7.6$; $N=11.8$ per cent.)

Dimethylaniline and Ethylene Dibromide.—The reaction in this case proceeded much more rapidly than with diethylaniline. A mixture of 188 grams of ethylene dibromide with 242 grams of dimethylaniline began to evolve methyl bromide after being heated for one hour at 180° , and the reaction was finished at the end of three and a-half hours.

Diphenyldimethylethylenediamine, $NMePh \cdot CH_2 \cdot CH_2 \cdot NMePh$, is the chief product of the reaction, and can be obtained in a yield of 73 per cent. by direct fractionation. It boils at $245^\circ/45$ mm., and forms prisms from light petroleum, which melt at 47° (compare Fröhlich, *Ber.*, 1907, **40**, 763; also Dunlop and Jones, *T.*, 1909, **95**, 418). (Found, $C=79.81$; $H=8.61$; $N=11.53$. $C_{16}H_{20}N_2$ requires $C=80.0$; $H=8.3$; $N=11.7$ per cent.)

The *picrate*, prepared in alcoholic solution, using excess of picric acid, melts and decomposes at 180° . From the following analysis, it would appear that this substance is the dipicrate:

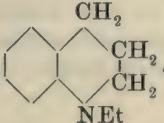
0.1763 gave 0.3105 CO_2 and 0.0601 H_2O . $C=48.03$; $H=3.79$.

$C_{16}H_{20}N_2 \cdot 2C_6H_3O_7N_3$ requires $C=48.1$; $H=3.7$ per cent.

Diphenylpiperazine can be isolated in the manner already described from the residue left after distilling the base; it is present in only small quantities. The transformation of diphenyldimethylethylenediamine into diphenylpiperazine and methyl bromide is, however, practically complete when the aniline derivative is heated with a molecular amount of ethylene dibromide at 190° for three hours.

Diethylaniline and Trimethylene Bromide.—As mentioned in the introduction (p. 1603), the reactions between the dialkylanilines and trimethylene bromide may be made to pursue either one of two courses, namely: (a) yielding the alkyl derivatives of tetrahydroquinoline, when the reacting mixture is immediately heated; (b) yielding the alkyl derivative of diphenyltrimethylenediamine when the mixture is allowed to remain previous to being heated.

(a) A mixture of 300 grams of trimethylene bromide and 450 grams of diethylaniline was heated at 180° , when the evolution of ethyl bromide commenced after half an hour. At the end of two and a-half hours 155 grams had been collected, the theoretical amount for the formation of the quinoline derivative being 161 grams.

N-Ethyl-1:2:3:4-tetrahydroquinoline, . — It was

not found possible to separate this base from the unchanged diethylaniline by distillation, and therefore the product of the reaction, after being treated with dilute alkali, was extracted with ether, and the whole of the bases present in the ether were extracted by shaking with dilute hydrochloric acid. It was then found that when the hydrochloric acid solution was mixed with an aqueous solution containing sufficient sodium acetate to react with the amount of hydrochloric acid used in the extraction, the whole of the quinoline base was precipitated, leaving the diethylaniline in the solution as acetate.

N-Ethyltetrahydroquinoline has been prepared by several investigators (Wischnegradsky, *Ber.*, 1880, **13**, 2400; Claus and Stegelitz, *ibid.*, 1884, **17**, 1329; Baillie and Tafel, *ibid.*, 1899, **32**, 73; Decker and Wisloki, *ibid.*, 1903, **36**, 2572). We find it to boil at 257—258°/758 mm. (Found, C=81·77; H=9·33; N=8·93. $C_{11}H_{15}N$ requires C=82·0; H=9·3; N=8·7 per cent.) For the purpose of identification, we have prepared the *platinichloride*, which decomposes at 160° (Found, Pt=26·53. $C_{11}H_{15}N, H_2PtCl_6$ requires Pt=26·63 per cent.); the *methiodide*, decomposing at 179° (Found, I=41·86. Calc., I=41·9 per cent.); and the *picrate*, melting at 117° (Found, N=14·5. Calc., N=14·4 per cent.). We find, however, that the best way to identify this base is through the *dinitro*-derivative, which is precipitated in yellow needles when the base is mixed with a large excess of dilute nitric acid (D 1·3). The compound crystallises from alcohol and melts at 120°:

0·1185 gave 0·2277 CO_2 and 0·0572 H_2O . C=52·40; H=5·36.

0·1001 „ 15·0 c.c. N_2 at 12·5° and 741 mm. N=16·80.

$C_{11}H_{14}O_4N_3$ requires C=52·6; H=5·2; N=16·7 per cent.

The amount of diphenyldiethyltrimethylenediamine formed under the above experimental conditions is too small to be isolated.

(b) *Diphenyldiethyltrimethylenediamine*,



—This compound occurs as the chief product in the reaction between trimethylene bromide and diethylaniline, if the reacting substances, in the same proportion as in the preceding experiment, are allowed to remain for thirty-six hours prior to being heated at 180°. The evolution of ethyl bromide commenced almost at once, and at the end of three hours 238 grams had been collected (theory for dianiline derivative=322 grams). The weaker bases were then separated from the small amount of unchanged diethylaniline by means of sodium acetate as in the former experiment, and fractionated under diminished pressure. A considerable quantity of ethyltetrahydroquinoline passed over below 200°/30 mm., but

the larger amount distilled at 245—247° as a viscid, pale yellow oil. (Found, C=80·73; H=9·31. $C_{19}H_{26}N_2$ requires C=80·8; H=9·3 per cent.)

The base has been prepared by Fröhlich (*Ber.*, 1907, **40**, 764); we find that the *picrate*, prepared in alcoholic solution, using excess of picric acid, and which melts and decomposes at 177°, is the dipicrate:

0·1857 gave 0·3419 CO_2 and 0·0729 H_2O . C=50·21; H=4·36.

$C_{19}H_{26}N_2 \cdot 2C_6H_3O_7N_3$ requires C=50·3; H=4·3 per cent.

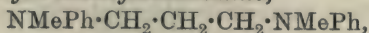
Dimethylaniline and Trimethylene Bromide.—In this case the tendency to form the diquaternary salt is so considerable (see p. 1603) that even when the mixture is immediately heated, considerable quantities of the dianiline derivative are produced.

(a) A mixture of 202 grams of trimethylene bromide and 242 grams of dimethylaniline was heated in the oil-bath. At 165° the content of the flask became practically solid owing to the separation of the mixed quaternary salts (see next section). At 180° methyl bromide began to be evolved; it was identified by passing it into an alcoholic solution of dimethylaniline and isolating the quaternary salt; needles, decomposing at 214—215°. (Found, Br=36·93. $C_9H_{14}NBr$ requires Br=37·0 per cent.)

At the end of three hours the contents of the flask had become liquid, and, calculated from the loss in weight. 135 grams of methyl bromide had been evolved, the theory for the quinoline derivative being 95 grams, and for the dianiline compound, 190 grams.

N-Methyl-1:2:3:4-tetrahydroquinoline (kairolin), boiling at 256—258°/756 mm., was the chief product isolated on fractionating the bases. (Found, C=80·47; H=8·80; N=9·53. $C_{10}H_{13}N$ requires C=80·6; H=8·8; N=9·5 per cent.) The base has been prepared by numerous investigators; it was characterised by the formation of the *dinitro*-derivative, yellow prisms, melting at 145—146° (Found, N=17·87. $C_{10}H_{11}O_4N_3$ requires N=17·7 per cent.); the *methiodide*, needles, decomposing at 172° (Found, I=43·90. Calc., I=43·94 per cent.); the *picrate*, yellow needles, melting at 123—124° (Found, N=14·78. $C_{10}H_{13}N \cdot C_6H_3O_7N_3$ requires N=14·9 per cent.); and the *platinichloride*, salmon-pink, crystalline powder (Found, Pt=27·64. $(C_{10}H_{13}N)_2 \cdot H_2PtCl_6$ requires Pt=27·7 per cent.).

Diphenyldimethyltrimethylenediamine,



distils at 245—247°/21 mm., and when recrystallised from light petroleum forms prisms melting at 47°. (Found, C=80·19;

$H=8.57$; $N=11.12$. $C_{17}H_{22}N_2$ requires $C=80.3$; $H=8.7$; $N=11.0$ per cent.) The base has been prepared by Fröhlich (*Ber.*, 1907, **40**, 764), who isolated the monopicrate by using one equivalent of picric acid. This base is, however, better adapted for the formation of crystalline derivatives than the other members of the series, and the isolation of the following compounds shows that a base of this character readily forms derivatives with two equivalents of an additive reagent.

The *dipicrate*, prepared in alcoholic solution, is a pale yellow, crystalline powder, which melts and decomposes at $189-190^\circ$:

0.1574 gave 0.2819 CO_2 and 0.0566 H_2O . $C=48.84$; $H=4.00$.

$C_{17}H_{22}N_2 \cdot 2C_6H_3O_7N_3$ requires $C=48.9$; $H=3.8$ per cent.

The *dioxalate* is prepared in alcoholic solution, and is precipitated on the addition of dry ether. It forms needles from alcohol, which melt at $146-147^\circ$:

0.1404 gave 0.2989 CO_2 and 0.0755 H_2O . $C=58.19$; $H=5.99$.

$C_{17}H_{22}N_2 \cdot (H_2C_2O_4)_2$ requires $C=58.1$; $H=6.0$ per cent.

The *dimethiodide*, prepared in ethereal solution, separates from alcohol in long, colourless needles, melting and decomposing at 216° :

0.2408 gave 0.2099 AgI . $I=47.11$.

$C_{17}H_{22}N_2 \cdot 2MeI$ requires $I=47.2$ per cent.

The *platinichloride*, prepared in the usual way, is a pale pink, crystalline powder:

0.2083 gave 0.0607 Pt . $Pt=29.01$.

$C_{17}H_{22}N_2 \cdot H_2PtCl_6$ requires $Pt=29.36$ per cent.

(b) In this case the mixture, as in experiment (a), was allowed to remain for thirty-six hours, and then heated on the water-bath for one hour. The partly solid mass was then collected and washed with dry ether. It was further purified by solution in alcohol and reprecipitation by pure ether, and was obtained as a white, deliquescent, crystalline powder, readily soluble in water:

0.3928 gave 0.3104 $AgBr$. $Br=33.62$ (precipitable).

The quaternary salt, $NMe_2PhBr \cdot CH_2 \cdot CH_2 \cdot CH_2Br$, contains 24.77 per cent. of precipitable bromine, whereas the salt, $NMe_2PhBr \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NMe_2PhBr$, contains 36.04 per cent. of precipitable bromine. It is evident therefore that the quaternary salt is a mixture containing a larger proportion of the quaternary salt of the dianiline derivative than of the salt yielding the quinoline derivative.

This view was supported by the fact that when the mixture was heated at 180° until methyl bromide ceased to be evolved, the

product was found to contain only a small quantity of methyl-tetrahydroquinoline, and to consist for the most part of diphenyl-dimethyltrimethylenediamine.

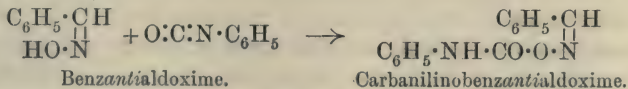
THE SORBY RESEARCH LABORATORY,
THE UNIVERSITY, SHEFFIELD.

CLXXV.—*The Isomerism of the Oximes. Part I.* *The Diphenylcarbamoyloximes.*

By OSCAR LISLE BRADY and FREDERICK PERCY DUNN.

THE action of phenylcarbimide on isomeric oximes has been studied by Goldschmidt and his collaborators (*Ber.*, 1889, **22**, 3112; 1890, **23**, 2136; 1891, **24**, 2546; 1893, **26**, 2087), by Beckmann (*Ber.*, 1890, **23**, 3321), and others.

In accordance with the Hantzsch-Werner hypothesis, the action has been represented as follows:



and



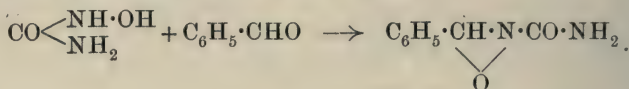
These compounds are readily decomposed by alkali hydroxides, the *anti*-compounds yielding aniline, carbon dioxide, and the *anti*-oxime, whilst the *syn*-compounds give aniline, carbon dioxide, a small quantity of diphenylcarbamide, the *syn*-oxime, and the nitrile.


In two cases three carbanilino-oximes, corresponding with one aldehyde, have been described, namely, two isomeric carbanilino-derivatives have been obtained from benzsynaldoxime and one from benzantialdoxime, whilst *m*-nitrobenzantialdoxime gives two carbanilino-oximes and *m*-nitrobenzsynaldoxime another.

There is at present no wholly satisfactory explanation of the existence of the third isomeride, and the authors hope in a subsequent communication to throw more light on this question. Conduché (*Ann. Chim. Phys.*, 1907, [viii], **12**, 533; 1908, [viii], **13**, 1), by the interaction of isohydroxycarbamide and aldehydes,

obtained the same compounds as by the action of isocyanic acid on the corresponding oximes.*.

Conduché represented the action thus:



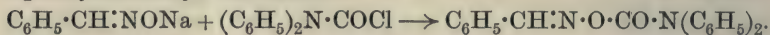

 Benzylidenecarbamidoxime.

He considered that his compounds were derivatives of the *syn*-oximes, as on treatment with hydrochloric acid the nitriles were obtained, although alkalis yielded the *anti*-oximes.

Beck and Hase (*Annalen*, 1907, **355**, 50) by the action of phenylhydroxycarbamide on *m*-nitrobenzaldehyde obtained the same compound as had been obtained previously by Goldschmidt (*loc. cit.*) by the action of phenylcarbimide on *m*-nitrobenzanti-aldoxime. As in this case the corresponding *syn*-derivative had been obtained, it was obvious that this compound could not have the *syn*-structure, so it was considered to have the constitution $\text{NO}_2 \cdot \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{N} \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$.

It seemed unlikely that the unsubstituted hydroxycarbamide would behave differently as stated by Conduché, and it was with the object of elucidating this matter that the present investigation was undertaken.

When phenylcarbimide is condensed with the oximes, or the hydroxycarbamides with the aldehydes, there is a considerable rearrangement in the molecule, whilst by the action of diphenylcarbamyl chloride on the sodium salt of the oxime this could be avoided, and little doubt left as to the structure of the resulting diphenylcarbamyl derivative:




The authors have accordingly prepared by this method the diphenylcarbamyl derivatives of benzaldoxime and of the three nitrobenzaloximes, and studied their properties.

It was found that identical products were obtained by the action of diphenylcarbamyl chloride on the sodium salts of both *anti*- and *syn*-oximes. In the case of the preparation from the *syn*-oximes, the reaction was carried out in the cold in dry non-aqueous solvents to avoid isomeric change as much as possible.

It has been shown (Goldschmidt, *Ber.*, 1895, **28**, 2013) that the formation of sodium salts from *syn*-oximes does not at once bring

* Conduché and Beck and Hase adopt Beckmann's *iso*-oxime formula, $\text{R} \cdot \text{CH} \cdot \text{NH}$,


 for the *syn*-oximes. In this paper, to avoid confusion, the generally accepted terms *anti* and *syn* are used throughout, the *anti*- and *syn*-oximes corresponding with the α - and β -oximes of Beckmann and his followers.

about isomeric change into the *anti*-form, a result confirmed by the present authors in the case of *m*-nitrobenzsynaldoxime. The sodium salt from *o*-nitrobenzsynaldoxime mentioned in a previous communication (P., 1911, **27**, 239) as consisting mainly of "*anti*" salt had been obtained as an oil and left for several days to crystallise, during which time isomeric change had probably taken place. The subject of the salts of the oximes is, however, being further investigated.

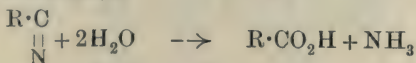
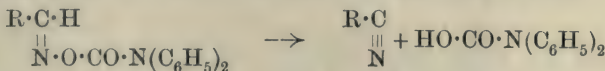
The behaviour of the diphenylcarbamyI derivatives on treatment with alkalis pointed to their having the *syn*-configuration, and the authors have accordingly assigned to them the structural formula:



DiphenylcarbamyIbenzsynaldoxime, $\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{N}\cdot\text{O}\cdot\text{CO}\cdot\text{N}(\text{C}_6\text{H}_5)_2$, on heating with alcoholic potassium hydroxide, is decomposed into diphenylamine, carbon dioxide, and benzonitrile.

In the case of the diphenylcarbamylnitrobenzsynaldoximes, it was found impossible to separate the nitrile from the other products of the reaction, but by heating for an hour with 2 per cent. alcoholic potassium hydroxide under reflux, these compounds were decomposed into carbon dioxide, diphenylamine, a small quantity of diphenylurethane, ammonia, and the corresponding acid, there being no evidence of the formation of oxime or aldehyde.

The production of diphenylurethane and the failure to obtain any trace of oxime lead the authors to consider that these compounds behave similarly to the acetyl derivatives of the *syn*-oximes, and that their decomposition may be represented thus:



It seems probable that the compounds obtained by Conduché from the aldehydes and hydroxycarbamide are not derivatives of the *syn*- but of the *anti*-oximes, especially in view of the production of *anti*-oxime and not of nitrile by the action of alkalis.

It is true that he obtained the nitriles on treatment of his compounds with hydrochloric acid, but the authors have been able to show that the carbanilino-derivatives of the *anti*-oximes where the isomeric *syn*-compounds are known yield with hydrochloric acid the corresponding benzoic acid, ammonium chloride, and

aniline hydrochloride, but no oxime, indicating the formation of nitrile and its subsequent hydrolysis.

The carbanilino-derivatives are more difficult to decompose than the unsubstituted carbamyl compounds, and the more vigorous treatment needed to decompose them with hydrochloric acid would account for the disappearance of the *syn*-oxime and nitrile obtained by Conduché from his compounds. It may be noted that the diphenylcarbamyl oximes are still more difficult to decompose. The action of hydrochloric acid can be understood when it is realised that the *anti*-aldoximes are converted into the *syn*-aldoximes by excess of hydrochloric acid in aqueous solution (Dunstan and Thole, P., 1911, 27, 233), an observation repeated and confirmed by the authors in the case of benzaldoxime and *m*-nitrobenzaldoxime.

Conduché has prepared the same carbamyl oxime from benz*anti*- and benz*syn*-aldoxime, this being apparently the only case in which he investigated the action of isocyanic acid on both isomerides. He, however, treated the hydrochloride of the *syn*-oxime with an aqueous solution of potassium cyanate, under which conditions there are ample opportunities for isomeric change.*

In conclusion, the authors consider that their work, which is being continued, tends to confirm still further the Hantzsch-Werner hypothesis of the isomerism of the oximes.

EXPERIMENTAL.

Diphenylcarbamylbenzsynaldoxime.—Benzantialdoxime (5 grams) was treated with sufficient sodium (0.895 gram) dissolved in alcohol to form the sodium salt, and the alcohol evaporated. The sodium salt was suspended in dry chloroform, and an equivalent quantity of diphenylcarbamyl chloride (9.0 grams) added, and the mixture heated for four hours under reflux. The liquid was then filtered, the chloroform evaporated, and the residue crystallised from hot alcohol:

0.1964 gave 15.2 c.c. N₂ at 19° and 759 mm. N=9.1.

C₂₀H₁₆O₂N₂ requires N=8.86 per cent.

Diphenylcarbamylbenzsynaldoxime is obtained in this way as a white, crystalline solid, which melts over a range of about 10° according to the rate of heating, as do all the diphenylcarbamyl oximes examined. By means of the Maquenne block, however, sharp and constant melting points could be obtained, and those given in this paper were determined by this method. The above compound melts on the Maquenne block at 163°.

* The authors hope to investigate the action of anhydrous isocyanic acid on the oximes and of carbamyl chloride on the sodium salts of the oximes.

The sodium salt of benzsynaldoxime was treated with diphenylcarbamyl chloride in dry ether in the cold for four days. The liquid was filtered, and the residue extracted with alcohol, from which crystals were obtained which proved to be identical with the compound described above.

Action of Alcoholic Potassium Hydroxide on Diphenylcarbamylbenzsynaldoxime.

The substance was heated under reflux for ten minutes with alcoholic potassium hydroxide, at the end of which time the liquid had a strong odour of benzonitrile. The alcohol was removed and the liquid filtered. The solid, after recrystallising, melted at 54° , and was diphenylamine. The filtrate was saturated with sulphur dioxide, to prevent benzaldehyde distilling should it have been formed, and distilled in a current of steam. The distillate still had a strong odour of benzonitrile. It was extracted with ether, and after evaporating off the ether an oil was left which, on boiling with potassium hydroxide, evolved ammonia, benzoic acid being recovered from the alkaline solution.

Preparation of the Sodium Salts of the Nitrobenzaldoximes.

It was found that the most convenient method for the preparation of the dry sodium salts of the nitrobenzaldoximes was to dissolve the oxime in much dry ether and add a slight excess of sodium ethoxide dissolved in the smallest possible quantity of alcohol. The solution was stirred vigorously for some minutes, when the sodium salt crystallised and could be easily collected. After being washed with dry ether and left on the filter for a few moments, the salt was quite dry.

Diphenylcarbamyl-p-nitrobenzsynaldoxime.—Equivalent quantities of diphenylcarbamyl chloride and of the sodium salt of *p*-nitrobenzantialdoxime were suspended in chloroform, and heated under reflux for four hours. The mixture was filtered, the chloroform evaporated, and the pale yellow residue of the carbamyl-oxime recrystallised from alcohol:

0.1386 gave 14.5 c.c. N_2 at 25° and 742 mm. $N = 11.76$.

$C_{20}H_{15}O_4N_3$ requires $N = 11.63$ per cent.

Diphenylcarbamyl-p-nitrobenzsynaldoxime forms colourless prisms melting at 174° .

Diphenylcarbamyl-m-nitrobenzsynaldoxime.—This compound may be obtained from *m*-nitrobenzantialdoxime in a similar way to the above. It has also been obtained by treating the sodium salt of *m*-nitrobenzsynaldoxime with diphenylcarbamyl chloride in

ethereal solution, the mixture being shaken for three hours. After filtering, the solid is washed with water and crystallised from alcohol:

0.1280 gave 13.1 c.c. N_2 at 21° and 743 mm. $N=11.68$.

$C_{20}H_{15}O_4N_3$ requires $N=11.63$ per cent.

Diphenylcarbamylo-nitrobenzsynaldoxime crystallises in colourless needles, melting at 175° .

Diphenylcarbamylo-o-nitrobenzsynaldoxime.—This was prepared in a similar way to the para-compound from the sodium salt of *o*-nitrobenzantialdoxime and diphenylcarbamylo chloride:

0.1444 gave 14.8 c.c. N_2 at 21° and 747 mm. $N=11.75$.

$C_{20}H_{15}O_4N_3$ requires $N=11.63$ per cent.

This compound crystallises in colourless needles, melting at 159° .

The diphenylcarbamylnitrobenzsynaldoximes all rapidly develop a yellow colour on exposure to light. They are soluble in hot alcohol, acetone, chloroform, benzene, or ethyl acetate, but insoluble or very sparingly soluble in water, cold alcohol, ether, or light petroleum.

Action of Alcoholic Potassium Hydroxide on the Diphenylcarbamylnitrobenzsynaldoximes.

The diphenylcarbamyloximes were heated with 2 per cent. alcoholic potassium hydroxide under reflux; at the end of half an hour, there was a plentiful evolution of ammonia. When the mixture had been gently boiling for an hour it was cooled, diluted, and filtered. The residue was washed with cold alcohol; from the alcoholic solution diphenylamine was isolated, and the substance insoluble in the cold alcohol proved to be diphenylurethane (m. p. 72°).

The alkaline filtrate was extracted with ether to remove traces of diphenylamine, etc., acidified, and again extracted with ether. After removing the ether and recrystallising the residue once from alcohol, the pure acid was obtained corresponding with the diphenylcarbamylnitrobenzsynaldoxime taken. This was identified by its melting point and the mixed melting point with the acid obtained by oxidising the corresponding nitrobenzaldehyde.

Action of Hydrochloric Acid on Carbanilino-p-nitrobenzantialdoxime.

Carbanilino-*p*-nitrobenzantialdoxime was heated for an hour with concentrated hydrochloric acid under reflux. The solution was diluted, made alkaline with potassium hydroxide, and filtered. On gently warming a portion of the alkaline liquid, there was a

copious evolution of ammonia, indicating the presence of an ammonium salt. The bulk of the alkaline liquid was extracted with ether to remove aniline, etc., acidified, and again extracted with ether. After removing the ether, a yellow solid remained, which, after recrystallising from alcohol, proved to be *p*-nitrobenzoic acid.

In conclusion the authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed the expenses of these experiments.

ROYAL COLLEGE OF SCIENCE,
SOUTH KENSINGTON,

CLXXVI.—*The Isomerism of the Oximes. Part II.*
The Nitrobenzaldoximes.

By OSCAR LISLE BRADY and FREDERICK PERCY DUNN.

CIAMICIAN and Silber (*Ber.*, 1903, **36**, 4268) have investigated the action of light on the three nitrobenzantialdoximes. They found that when these substances were suspended in benzene in sealed tubes and exposed to sunlight, *o*- and *p*-nitrobenzantialdoximes were converted into the corresponding nitrobenzsynaldoximes; on the other hand, *m*-nitrobenzantialdoxime, as obtained from the aldehyde and hydroxylamine, remained unchanged. They therefore concluded that the nitrobenzaldoximes were stable in the *syn*-condition, and that the *m*-compound, as ordinarily obtained, was in the *syn*- and not the *anti*-form as usually supposed.

Goldschmidt (*Ber.*, 1904, **37**, 180) argued that *m*-nitrobenzantialdoxime could not have been assigned the wrong structural formula in view of other work on this compound and sought to provide some explanation of the exceptional result, without, however, repeating the work of Ciamician and Silber on the action of light. The fact that *m*-nitrobenzantialdoxime was found to behave differently from the *o*- and *p*-compounds seemed so extraordinary in view of the other properties of the nitrobenzaldoximes, that the authors thought it desirable to repeat this work, more especially as, apparently, the melting points of the compounds were solely relied on for their identification. The directions of Ciamician and Silber were followed, and it was found that after ten days all three nitrobenzantialdoximes had been partly converted into the corresponding nitrobenzsynaldoximes. The pre-

sence of these compounds was ascertained by means of their melting points, mixed melting points with pure nitrobenzsyn- and nitrobenzanti-aldoximes, and conversion into the nitriles by means of acetic anhydride as described by Hantzsch (*Ber.*, 1891, **24**, 17). It seems therefore that the three nitrobenzantialdoximes, on exposure to sunlight under certain conditions, undergo isomeric change into the nitrobenzsynaldoximes.

The action of light on the *O*-methyl ethers of the nitrobenzanti-aldoximes was also investigated, and here, too, the conversion took place, although less readily. Further research on the action of light on other derivatives of the aldoximes is at present in hand.

During this work it has been necessary to determine the configuration of the various products, and to have pure specimens of the *O*-methyl ethers of the nitrobenzsynaldoximes.

The acetyl derivatives of the nitrobenzsynaldoximes have been investigated by Hantzsch (*Zeitsch. physikal. Chem.*, 1894, **13**, 525), but those of the nitrobenzantialdoximes do not seem to have been described.

The authors have investigated the action of acetic anhydride on the nitrobenzsyn- and nitrobenzanti-aldoximes, and in the former case have obtained the nitriles as described by Hantzsch, and in the latter case have isolated the acetyl derivatives and recovered from them the nitrobenzantialdoximes; there seems no doubt, therefore, of the configuration of the six nitrobenzaldoximes.

It seemed possible that the *O*-methyl ethers of the nitrobenzsynaldoximes as previously obtained were mixtures of the two isomerides, so these compounds were also studied. It was found that the most convenient method for their preparation was to obtain as pure as possible a silver salt of the nitrobenzsynaldoxime, and shake this, suspended in ether, with methyl iodide. The *p*- and *m*-compounds obtained in this way melted at a slightly higher temperature than the compounds described in the literature.

<i>O</i> -Methyl ether	Recorded m. p.	M. p. (B. and D.)
<i>o</i> -Nitrobenzsynaldoxime	Oil	Oil
<i>m</i> -Nitrobenzsynaldoxime	69°	74°
<i>p</i> -Nitrobenzsynaldoxime	67—68°	70°

The *O*-methyl ether of *p*-nitrobenzsynaldoxime was fractionally crystallised several times, two solvents being used; the various fractions melted from 67° to 70°, and hence there was little doubt that this substance had been obtained pure. The authors are unable to accept the view of Ciamician and Silber that the nitrobenzaldoximes are "*syn*" stable (compare Goldschmidt, *loc. cit.*), the readiness with which the nitrobenzsynaldoximes are converted into the corresponding antialdoximes being at variance with this

conclusion. Thus, *o*-nitrobenzsynaldoxime (Goldschmidt and van Rietschoten, *Ber.*, 1893, **26**, 2100) and *m*-nitrobenzsynaldoxime are converted into the *antialdoximes* by warming for some time with benzene. Goldschmidt has shown that this also partly takes place in the case of the *m*-compound by using dry ether at 25°. Forster and Dunn (T., 1909, **95**, 425) have shown that the nitrobenzsynaldoximes are partly transformed into the *antialdoximes* even in cold non-aqueous solvents. The authors have studied the isomeric change of the nitrobenzsynaldoximes into the corresponding *antialdoximes* in acetone solution. There is no ready method of estimating the amount of the two isomerides present, but a study of the melting points of the mixtures gives some idea of this.

The change was investigated by dissolving equal amounts of the oximes in acetone and precipitating equal volumes from time to time with ten times their volume of water (in the case of the *m*-compound with twenty times), and determining the melting points of the products; the results may be tabulated thus*:

Time.	<i>o</i> -Nitrobenz- synaldoxime, m. p. 154°. <i>anti</i> -, m. p. 102°.	<i>m</i> -Nitrobenz- synaldoxime, m. p. 123°. <i>anti</i> -, m. p. 120°.	<i>m</i> -Nitrobenz- synaldoxime mixed with <i>anti</i> -. <i>anti</i> -, m. p. 129°.	<i>p</i> -Nitrobenz- synaldoxime, m. p. 184°. <i>anti</i> -, m. p. 129°.
1 minute	150°	123°	97°	180°
15 minutes	146	118	96	170
30 „	146	118	94	164
45 „	146	117	95	164
1 hour	146	118	93	163
3 hours	146	115	97	162
14 „	135	114	95	157
38 „	—	114	95	155

A portion evaporated to dryness by a stream of dry air.

38 hours	122°	113°	96°	144°
62 „	89	112	98	125

The authors had in their possession several specimens of pure, nitrobenzsynaldoximes, which had been preserved for some years in stoppered bottles in the dark; the melting points of these compounds were taken with the following results:

* Owing to the greater solubility of the nitrobenzantiaaldoximes in a mixture of acetone and water, it is probable that the oxime was not completely precipitated even at this dilution, especially in view of the much larger depression of the melting point obtained when the solution was evaporated to dryness and the residue examined. The figures given are for the complete liquefaction of the substance, which at first sintered over about five degrees, but after fourteen hours over fifteen to twenty degrees. It was necessary to take mixed melting points in the case of the *m*-compound owing to the *anti*-melting so near the *syn*-compound.

	M. p. at time of preparation.	M. p. after four years.	M. p. of <i>anti</i> -compound.
<i>o</i> -Nitrobenzsynaldoxime	154°	135—139°	102°
<i>p</i> -Nitrobenzsynaldoxime	182—184	155—160	129
<i>m</i> -Nitrobenzsynaldoxime	123	118—119	120
<i>O</i> -Methyl ether of <i>m</i> -nitro- benzsynaldoxime	74	74	101

The same specimen of *p*-nitrobenzsynaldoxime two years after preparation melted at 175°; the *O*-methyl ether examined, mixed with *anti*-compound, melted at 45°. The *m*-nitrobenzsynaldoxime examined proved to have been entirely transformed into the *anti*-compound, as it no longer depressed the melting point of this substance. It seems therefore that even in the solid state the nitrobenzsynaldoximes are slowly converted into the nitrobenz*anti*aldoximes, but that the *O*-methyl ethers are more stable; moreover, the *syn*-oximes change to the *anti*-form at their melting point, a change not observed in the case of the *O*-methyl ethers.

Experiments were undertaken to ascertain if, in the case of the nitrobenzaldoximes, any *syn*-oxime is produced by the action of hydroxylamine on the aldehyde. Bamberger and C. Goldschmidt (*Ber.*, 1894, **27**, 3428) have shown that by the action of hydroxylamine on cinnamaldehyde a mixture of *anti*- and *syn*-oximes is produced, and Forster and Dunn (*loc. cit.*) obtained α -benzilmonoxime by the action of hydroxylamine on benzil in pyridine. This result led the authors to investigate the action of hydroxylamine on *o*-nitrobenzaldehyde in various solvents. The solvents used were alcohol, chloroform, pyridine, ether, and benzene, but in no case could the formation of *syn*-oxime be detected.

Luxmore (*T.*, 1896, **69**, 177) has obtained two hydrochlorides of benzaldoxime, one of which, on treatment with ammonia and ice, regenerates the *anti*-oxime, the other yielding the *syn*-compound. Attempts were made to isolate a second hydrochloride of *p*-nitrobenzaldoxime, but without success, the reaction being tried in the light and in the dark, at room temperature and at 0°.

It is of interest that the hydrochloride at its melting point yields the *anti*-oxime, and if left exposed to moist air in the dark after some time loses hydrogen chloride and gives the *anti*-oxime. If, however, it is left in a desiccator in the dark, it loses hydrogen chloride, and leaves a mixture of *anti*- and *syn*-oxime.

EXPERIMENTAL.

Preparation of the Nitrobenzsynaldoximes.—As considerable quantities of pure *syn*-aldoximes were required for these investigations, the various methods for the preparation of these compounds have been tried. Dunstan and Thole (*P.*, 1911, **27**, 233) have

described a method for the preparation of *m*-nitrobenzsynaldoxime, which proved to be the most convenient, and has been found to work equally well with the *o*- and *p*-compounds. In the case of *o*-nitrobenzaldoxime, however, the hydrochloride was completely soluble in the saturated aqueous solution of hydrochloric acid, whilst the hydrochloride of *p*-nitrobenzaldoxime, like that of the *m*-compound, was sparingly soluble, if at all.

It is noteworthy that the nitrobenzaldoximes and their derivatives may be most conveniently purified by solution in acetone, followed by cautious addition of water with constant stirring; in this way, the compound is precipitated in a crystalline condition. The *syn*-derivatives are less soluble than the *anti*-compounds, and the authors have obtained consistently good results by this method.

The Action of Light on the Nitrobenzantialdoximes.

Two grams of *p*-nitrobenzantialdoxime in 40 c.c. of benzene, 2.5 grams of *o*-nitrobenzantialdoxime in 50 c.c. of benzene, and 2.5 grams of *m*-nitrobenzantialdoxime in 200 c.c. of benzene were sealed in glass tubes and exposed to sunlight during ten days. At the end of that time the *o*- and *p*-compounds, owing to alternate warming and cooling, had formed large crystals on the sides of the tube; the *m*-compound, which remained completely in solution, when warm, contained brown flocks as described by Ciamician and Silber; these disappeared on cooling in the evening. As the *syn*-compounds are less soluble than the *anti*-, the crystals which separated were examined. In the case of the para-compound, the crude substance melted at 153°, and after recrystallisation from acetone and water at 175°. *p*-Nitrobenzantialdoxime melts at 129°, and the *syn*-compound, when pure, at 182–185°, although it is difficult to obtain a product melting above 177° (Forster and Dunn, T., 1909, 95, 426). The crude *o*-compound melted at 147°, and, mixed with pure *o*-nitrobenzsynaldoxime (m. p. 154°), at 150°.

The solution containing the *m*-nitrobenzaldoxime was evaporated by means of a current of air, and the first crop of crystals was examined. These melted at 120° (*syn*-compound, m. p. 123°), and, mixed with pure *m*-nitrobenzsynaldoxime and *m*-nitrobenzantialdoxime (m. p. 120°) at 121° and 90° respectively.

In each case the *syn*-derivative was treated with acetic anhydride, and the reaction mixture decomposed with sodium carbonate solution, when the corresponding nitrile was obtained, which, after one crystallisation from alcohol, melted at the correct temperature.

A second experiment was performed in the case of *m*-nitrobenz-

antialdoxime, 2 grams being suspended in 50 c.c. of benzene. After ten days large crystals had formed on the sides of the tube, which were examined as before, and found to consist of *m*-nitrobenz-*synaldoxime*.

A quantity of *o*-nitrobenz*antialdoxime* was heated in a sealed tube to 100° for four hours, but no trace of *syn*-oxime could be detected in the product.

The Action of Light on the O-Methyl Ethers of the Nitrobenzantialdoximes.—The *O*-methyl ethers of the three nitrobenz*antialdoximes* were dissolved in quantities of 1 gram in 10 c.c. of benzene, sealed in test-tubes, and exposed to sunlight during ten days. The benzene was then removed by a current of air, when in the case of the ortho-compound an uncrystallisable oil was obtained, which appeared to be the *syn*-derivative. The residue from the meta-compound was fractionally crystallised from acetone and water, and a substance melting at 68° was obtained; this, when mixed with the *O*-methyl ether of *m*-nitrobenz*synaldoxime* (m. p. 74°), melted at 70°, and with the ether of the *anti*-compound at 45°. The para-compound had not been so completely converted, the crude product melting at 80° (*anti*, m. p. 101°, *syn*, m. p. 70°). By fractional crystallisation this was, however, divided into two portions, melting respectively at 90° and 68°, the substance obviously being a mixture of the two isomerides. Although the *O*-methyl ethers of the nitrobenz*antialdoximes* are converted by the action of light into the corresponding *syn*-derivatives, the action is much slower than in the case of the oximes themselves.

Preparation of the Acetyl Derivatives of the Nitrobenzantialdoximes.

These compounds were obtained by adding to the nitrobenz*antialdoximes* sufficient acetic anhydride to dissolve them completely on gentle warming. After ten minutes the mixture was shaken with concentrated sodium carbonate solution until the excess of acetic anhydride had been decomposed. The solid acetyl compound remaining was collected and crystallised from acetone and water.

Acetyl-o-nitrobenzantialdoxime forms colourless needles, melting at 66°:

0.1336 gave 16.0 c.c. N₂ at 22° and 750 mm. N=13.74.

C₉H₈O₄N₂ requires N=13.46 per cent.

Acetyl-m-nitrobenzantialdoxime forms fine, colourless needles, melting at 128°:

0.1566 gave 18.8 c.c. N₂ at 25° and 755 mm. N=13.72.

C₉H₈O₄N₂ requires N=13.46 per cent.

Acetyl-p-nitrobenzantialdoxime forms pale yellow plates, melting at 127°:

0.2037 gave 24.5 c.c. N_2 at 25° and 753 mm. $N=13.70$.

$C_9H_8O_4N_2$ requires $N=13.46$ per cent.

These compounds, on treatment with dilute alkali for twenty-four hours, gave theoretical quantities of the corresponding nitrobenzantialdoximes. The three nitrobenzsynaldoximes were acetylated in a similar way, and in each case an almost theoretical yield of the corresponding nitrile was obtained.

Preparation of the O-Methyl Ethers of the Nitrobenzsynaldoximes.

The sodium salts of the nitrobenzsynaldoximes were obtained as previously described (compare Brady and Dunn, this vol., p. 1617); these were dissolved in water, and an excess of a concentrated solution of silver nitrate at once added. The silver salt thus precipitated was collected, washed with water, and dried as rapidly as possible on a porous plate. When dry, this was suspended in dry ether, and shaken for ten minutes with excess of methyl iodide, at the end of which time the liquid was filtered, the ether evaporated by a current of dry air, and the residue fractionally crystallised from acetone and water. The *o*-compound was invariably obtained as an oil, which did not crystallise even at -20°; the *p*-compound was found to melt at 70°, and the *m*-compound* at 74°, several degrees higher than is recorded in the literature. The *p*-methyl ether was fractionally crystallised to test, to some extent, its purity. Seven fractions were re-crystallised from alcohol and water, and were found to melt between 67° and 70°, the least soluble portions having the higher melting point. The fractions melting at 70° were then re-crystallised from acetone and water, the first two fractions melting at 70°, and the third at 68°.

Influence of Solvents on the Formation of o-Nitrobenzaldoxime.

The quantities of aldehyde and of hydroxylamine used in each experiment were in the ratio of 1 molecule of the former to 2½ molecules of the latter. The hydroxylamine hydrochloride was ground with the solvent, and a sufficient quantity of pure dry sodium ethoxide added to decompose the hydrochloride. The solution was then filtered and added to the solution of the aldehyde in the same solvent. The solvents used were alcohol, chloroform, ether, benzene, and pyridine. Alcohol was used as solvent in two

* Melting points of the *anti*-ether, mixture of *anti*- and *syn*-ethers, and of *syn*-ether were 65°, 47°, and 74° respectively.

experiments, in one of which sufficient sodium ethoxide was added to form the sodium salt of the oxime. The mixture was kept for a week in a dark place, and any solid which had crept up the side of the containing vessel removed. This was found to be chiefly unchanged aldehyde. The solution was evaporated in a closed vessel by means of a current of dry air, and the residue dissolved in the least possible quantity of warm benzene, in which the *syn*-aldoxime is less soluble than the *anti*-aldoxime. The melting point of the first crystals which separated was determined, but in no instance was there any evidence of the formation of *syn*-aldoxime. In alcoholic solution complete oximation had taken place, but with the other solvents examined only a small quantity of aldehyde had been converted into *anti*-aldoxime.

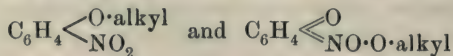
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CLXXVII.—*The Structure of the Salts of Nitrophenols.*

By JOHN THEODORE HEWITT, RHODA MARIANNE JOHNSON, and
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THE view originally put forward by Armstrong (P., 1888, **4**, 27; 1892, **8**, 101, 103, 143, 189, 194) that the salts of the nitrophenols differ in constitution from the parent substances, the latter having a benzenoid and the former a quinonoid configuration, has now received very general support. It must be admitted that the evidence is based chiefly on the marked change which takes place in the selective absorption on salt-formation. In fact, the present authors cannot recall any chemical evidence which has been adduced in support of the quinonoid rearrangement with the exception of the isolation of the strongly coloured *aci*-esters of certain nitrophenols by Hantzsch and Gorke (*Ber.*, 1906, **39**, 1073). The alkyl ethers of the nitrophenols and the deeply-coloured compounds referred to must be represented by such formulæ as:



respectively, the former being produced by direct nitration of aryl-alkyl ethers, and giving alkyloxylanilines on reduction; for the

latter no other structure appears possible; moreover, the structure assigned agrees with the ready hydrolysis of substances of this type.

The deep colour of both *aci*-esters and metallic salts leads to the assignment of a quinonoid structure for the latter; the argument is admittedly based on analogy.

Alteration in structure on salt-formation may, in certain cases, be followed chemically; a case in point is furnished by the hydroxyazo-compounds which, when subjected to the action of substituting reagents, behave as azophenols; their salts with mineral acids, however, as derived from arylhydrazones of quinones (T., 1900, **77**, 99, 712, 810).

Now whilst the nitrophenols exhibit phenolic reactions when treated with bromine, nitric acid, etc., it is evident that the action of such reagents on their salts or alkaline solutions is out of the question, and in order to obtain chemical evidence of essential structural difference between a pair of substances such as sodium phenoxide and sodium *o*- or *p*-nitrophenolate,* recourse must be had to some other sort of reaction. To establish the case for change in configuration taking place when a nitrophenol is converted into its sodium salt, it is necessary to show that (a) reactions associated with the group $\cdot\text{ONa}$ in compounds of the type of sodium phenoxide are wanting, (b) that in the nitrophenolate salts the reactions of the nitro-group are modified. As to reactions depending on the $\cdot\text{ONa}$ (or similar) group we have chosen those which take place with alkyl haloids, and the salts and esters of chloroacetic acid; for the diagnosis of the unaltered nitro-group, the production of azoxy-compounds on heating with sodium methoxide solution.

(a) *Reactions with Halogen Derivatives.*

Alkaline solutions of unsubstituted phenols react readily with alkyl haloids, giving good yields of mixed ethers (Cahours, *Compt. rend.*, 1851, **32**, 60; *Annalen*, 1851, **78**, 226).

The alkaline salts of the nitrophenols react less smoothly with alkyl haloids; thus, in order to prepare *o*-nitroanisole, Brunck (*Zeitsch. f. Chem.*, 1867, 204) used methyl iodide and silver nitrophenolate, whilst Mühlhäuser (*Annalen*, 1881, **207**, 237) heated 139 grams of *o*-nitrophenol, 57 grams of potassium hydroxide, and 142 grams of methyl iodide diluted with twice its volume of methyl alcohol under an excess pressure of 200 mm. of mercury for six hours, obtaining 72 per cent. of the theoretical yield.

* An excuse for the term "nitrophenolate" rather than "nitrophenoxide" is that the latter term definitely commits one to a certain constitution of the salt.—J. T. H.

Alkaline solutions of phenols also react readily with the alkaline salts of chloroacetic acid; thus Giacosa (*J. pr. Chem.*, 1879, [ii], **19**, 396) obtained the sodium salt of phenoxyacetic acid by mixing 1 part of phenol with 1 part of chloroacetic acid, and adding 4 parts of sodium hydroxide solution (D 1.3), the reaction taking place rapidly. Thate (*J. pr. Chem.*, 1884, [ii], **29**, 148) found that a mixture of 1 molecule of *o*-nitrophenol, 1 molecule of chloroacetic acid, and 2 molecules of sodium hydroxide required ten to eleven hours' heating on the water-bath; Fritzsche (*J. pr. Chem.*, 1879, [ii], **20**, 290) obtained *p*-nitrophenoxyacetic acid from the sodium salts of *p*-nitrophenol and chloroacetic acid.

In carrying out reactions between the sodium salts of phenols and α -halogen-substituted aliphatic esters, absence of water is essential for a good yield. By adding 1 molecule of a phenol to an atom of sodium dissolved in absolute alcohol, and then 1 molecule of ethyl chloroacetate, sodium chloride begins to separate almost immediately, and warming for one hour or so on the water-bath ensures a nearly quantitative reaction. A quite different state of affairs is seen in the case of the *o*- and *p*-nitrophenols.

Auwers and Haymann (*Ber.*, 1894, **27**, 2805) were unable to bring about a reaction between ethyl chloroacetate and the sodium salts of *o*- and *p*-nitrophenol. Steric hindrance cannot be the only factor coming into play, since *o*-bromophenol gives a good yield of ethyl *o*-bromophenoxyacetate (*loc. cit.*, p. 2799). Kym, however, obtained good yields of the *o*- and *p*-nitro-esters by heating the dry nitrophenolates with ethyl chloroacetate for some hours at 180° (*J. pr. Chem.*, 1897, [ii], **55**, 113, 122), and Bischoff (*Ber.*, 1900, **33**, 254) heated the dry sodium salts of the nitrophenols with the α -bromo-derivatives of propionic, butyric, *isobutyric*, and *isovaleric* acids. In order to obtain satisfactory yields, a higher temperature than that of the water-bath as well as dryness of the materials was necessary.

To apply the reaction between ethyl chloroacetate and the sodium derivatives of phenols as a test for the :C·ONa-group, we have used a number of phenols, some of which had been previously examined, others which had so far not been converted into aryl-oxyacetic esters. It may be at once remarked that the reaction proceeds smoothly and rapidly in the case of phenol and the cresols, rather more slowly but with no particular difficulty in the case of halogen-substituted phenols; *m*-nitrophenol may be normally converted with fair yield into ethyl *m*-nitrophenoxyacetate; but despite the greatest care, we were unable to isolate the isomeric *o*- and *p*-nitrophenoxyacetic esters by starting with the

sodium derivatives of *o*- and *p*-nitrophenols, and heating at water-bath temperature. These salts of phenols substituted by a nitro-group in the *o*- or *p*-position behave so differently chemically that we must conclude that the grouping :C:ONa is wanting. The actual course of the reaction in the case of the sodium salts of various phenols will now be described.

Phenol.—Ethyl phenoxyacetate has been obtained by esterification of the acid (Fritzsche). Homologous esters have been obtained by Bischoff (*Ber.*, 1900, **33**, 924) from dry sodium phenoxide and ethyl bromopropionate, etc.

0.92 Gram of sodium was dissolved in 20 c.c. of absolute alcohol, then 3.76 grams of phenol were added, and the mixture was warmed until the solution was uniform. Ten c.c. of an absolute alcoholic solution of ethyl chloroacetate were added, containing 4.9 grams of the ester. Sodium chloride separated almost immediately in the cold. After one hour's heating on the water-bath the mixture was diluted to 200 c.c. with water, and the unchanged phenol (0.1171 gram) estimated in 10 c.c. by bromine and thio-sulphate; thus altogether $0.1171 \times 20 = 2.342$ grams of phenol had escaped reaction, that is, 37.7 per cent. of the phenol had been converted into ethyl phenoxyacetate.

o-Cresol.—The methyl and tolyl esters of *o*-tolylxyacetic acid are known (Forte, *Gazzetta*, 1892, **22**, ii, 543; Farbenfabriken vorm. F. Bayer & Co., D.R.-P. 85490), and Bischoff (*Ber.*, 1900, **33**, 1249) has acted on dry sodium *o*-tolyl oxide with the ethyl esters of the α -bromo-substituted propionic, butyric, isobutyric, and isovaleric acids.

0.46 Gram of sodium and 2.16 grams of *o*-cresol in 10 c.c. of absolute alcohol were mixed with 2.45 grams of ethyl chloroacetate, made up to 5 c.c. with absolute alcohol. After one hour on the water-bath, the reaction was stopped, and unchanged *o*-cresol estimated by bromine and thiosulphate: 24.8 per cent. of the *o*-cresol had reacted.

In order to prepare *ethyl o-tolylxyacetate*, heating under reflux of quantities in the same proportions was continued for three hours; the whole was poured into water, the ester extracted with ether, the ethereal extract dried, and rectified. The ester is a liquid boiling at $248^\circ/752$ mm. (uncorr.):

0.1006 gave 0.2497 CO_2 and 0.0649 H_2O . C = 67.91; H = 7.17.

$\text{C}_{11}\text{H}_{14}\text{O}_3$ requires C = 68.07; H = 7.22 per cent.

m-Cresol.—The reaction of the sodium derivative with ethyl chloroacetate proceeds more rapidly than in the case of *o*-cresol. After one hour's heating under strictly parallel conditions, 44.8 per cent. was found to have reacted.

Ethyl m-tolyloxyacetate is a colourless liquid boiling at 251—252°/752 mm. (uncorr.); the method of preparation resembles that of the *o*-isomeride:

0.1638 gave 0.4078 CO₂ and 0.1058 H₂O. C=67.89; H=7.18.

C₁₁H₁₄O₃ requires C=68.07; H=7.22 per cent.

p-Cresol.—Under exactly similar conditions to those described above, sodium *p*-tolyloxyde reacts with ethyl chloroacetate to the extent of 46.2 per cent. in one hour.

Ethyl p-tolyloxyacetate is a liquid boiling at 243°/752 mm. (uncorr.):

0.1467 gave 0.3652 CO₂ and 0.0942 H₂O. C=67.90; H=7.14.

C₁₁H₁₄O₃ requires C=68.07; H=7.22 per cent.

Halogen-substituted Phenols.—The reaction of the sodium salts of various halogenated phenols has been examined by Auwers and Haymann (*loc. cit.*) and by Bischoff (*Ber.*, 1900, **33**, 1603).

We confined ourselves to 2:4:6-tribromophenol, as this is most likely to show the effects of steric hindrance.

Bischoff obtained the ethyl esters of 2:4:6-trichloro- and tribromo-phenoxyacetic acids by boiling the dry sodium salts of the trichloro- and tribromo-phenols with ethyl chloroacetate under reflux for two hours. We find that the reaction proceeds quite well in absolute alcoholic solution.

Quantities were taken proportionately to those mentioned for phenol and the cresols; on adding ethyl chloroacetate, sodium chloride began to separate immediately; in order to further the reaction, the mixture was heated between two and three hours on the water-bath. On pouring into water and extracting with ether, white crystals were obtained, which melted at 72°. After two crystallisations from light petroleum the melting point was found to be 79° (uncorr.). (Found, Br=57.48. Calc., 57.55 per cent.) Bischoff gives 81° as the melting point of ethyl 2:4:6-tribromophenoxyacetate.

o-Nitrophenol.—Kym (*J. pr. Chem.*, 1897, [ii], **55**, 123) heated dry sodium nitrophenolate with ethyl chloroacetate at 180°, and obtained ethyl *o*-nitrophenoxyacetate in quantitative yield. When, however, the reacting substances are heated in alcoholic solution on the water-bath, one is unable to isolate the ester.

5.56 Grams of *o*-nitrophenol and 0.92 gram of sodium in 20 c.c. of absolute alcohol were mixed with 4.9 grams of ethyl chloroacetate, made up to 10 c.c. with absolute alcohol. After one hour's boiling under reflux on the water-bath the alcohol was distilled off, a small quantity of potassium hydroxide added, and excess of ethyl chloroacetate removed in a current of steam. The residue in the

flask was acidified, and 5.42 grams of *o*-nitrophenol were recovered unchanged.

m-Nitrophenol.—1.84 Grams of sodium were dissolved in 40 c.c. of absolute alcohol and 11–12 grams of *m*-nitrophenol, and 9.8 grams of ethyl chloroacetate diluted with 20 c.c. of absolute alcohol successively added. After boiling for three hours under reflux, water was added, and the ester extracted with ether. The ethereal layer was repeatedly extracted with dilute sodium hydroxide solution until this no longer became coloured.

From the alkaline aqueous solution 4.2455 grams of *m*-nitrophenol were recovered by acidification with acetic acid, extraction with ether, and evaporation of the solvent.

The ethereal solution from which *m*-nitrophenol had been removed by the washing with sodium hydroxide was dried and fractionated under diminished pressure, when 6.7579 grams of a yellow, somewhat viscous liquid boiling at 208–212°/30 mm. were obtained:

0.0720 gave 0.1414 CO₂ and 0.0291 H₂O. C=53.54; H=4.79.

0.2033 „ 11.1 c.c. N₂ at 20° and 766 mm. N=6.41.

C₁₀H₁₁O₅N requires C=53.33; H=4.88; N=6.22 per cent.

One gram of the ester was hydrolysed by boiling for one hour under reflux with 0.5 gram of potassium hydroxide in 10 c.c. of alcohol. Water was added, the alcohol evaporated, and *m*-nitrophenoxyacetic acid obtained on acidification with hydrochloric acid. The acid forms very pale yellow needles, melting at 151° after repeated crystallisation from hot water:

0.0670 gave 5.55 c.c. N₂ at 22° and 764.5 mm. N=7.0.

C₈H₇O₅N requires N=7.1 per cent.

p-Nitrophenol.—2.78 Grams of *p*-nitrophenol were dissolved in 10 c.c. of sodium ethoxide solution (0.46 gram Na) and mixed with 5 c.c. of an absolute alcoholic solution of ethyl chloroacetate (2.45 grams). After three to four hours on the water-bath the product was worked up in the usual manner for the ethyl ester, but none was obtained. Ethyl *p*-nitrophenoxyacetate has been obtained by Kym (*loc. cit.*) by heating dry sodium nitrophenolate with ethyl chloroacetate at 180°.

4-Bromo-2-nitrophenol.—After one and a-half hours' heating in alcoholic solution under reflux, 4.30 grams out of 4.36 grams taken were recovered unchanged. In the case of 2:4- and 2:6-dinitrophenols no reaction between their sodium salts and ethyl chloroacetate by boiling in alcoholic solution could be detected.

(b) Reaction with Alkaline Reducing Agents.

Alkaline reduction of nitro-hydrocarbons leads to the production of azoxy-compounds; thus Zinin used alcoholic potassium hydroxide (*J. pr. Chem.*, 1845, **36**, 93), and Alexejew sodium amalgam (*Bull. Soc. chim.*, 1864, [ii], **1**, 324); the use of sodium methoxide (Klinger, *Ber.*, 1882, **15**, 866) seems to be most generally useful. Replacement of hydrogen by halogen or by an alkyloxy-group in no way hinders the reaction (Gattermann and Ritschke, *Ber.*, 1900, **23**, 1738), but nitrophenols are not converted into azoxy-compounds by heating with sodium methoxide.

One of the present authors, in conjunction with Dr. James Kenner, examined numerous nitrophenols in this respect some years ago, and in no case obtained any sign of formation of an azoxy-compound.

Hence it would appear that when an *o*- or *p*-nitrophenol is converted into a salt, the $\text{:C}\cdot\text{OH}$ group does not become $\text{:C}\cdot\text{ONa}$, whilst the nitro-group does not remain unchanged.

The authors desire to express their thanks to the Government Grant Research Committee for a grant, by which the expenses of this work have been defrayed.

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CLXXVIII.—*The Methylation of Quercetin.*

By ARTHUR GEORGE PERKIN.

WHEREAS in 1884 Herzig (*Monatsh.*, **5**, 72) observed that quercetin could not be completely methylated by means of methyl iodide and alkali, v. Kostanecki and Dreher, as the result of their experiments with the monohydroxyxanthenes (*Ber.*, 1893, **26**, 76), showed that although the methyl ethers of the 2-, 3-, and 4-compounds could be readily prepared by this method, the 1-hydroxyxanthone in which the hydroxyl is adjacent to the carbonyl group was thus not affected. In relation also to the dihydroxyxanthone, chrysin, Kostanecki states (*Ber.*, 1893, **26**, 2901), "Dass im Chrysin beim methyliren ein Hydroxyl unangeriffen bleibt . . . das Hydroxyl welches im Orthostellung steht, sich nicht methyliren lässt." Alizarin (Schunck and Marchlewski, *T.*, 1894, **65**, 185) behaves similarly, and, indeed, this property has been so generally observed in the case of aromatic hydroxy-ketones and acids that the resist-

ance of an hydroxyl group to methylation by this process has in many cases been considered to serve for the detection of a carbonyl group. Although ethyl iodide resembles methyl iodide in this respect, and it appears to have been generally considered that the complete ethylation of such hydroxy-compounds could not be effected by means of this reagent, certain exceptions in this case are to be found in the literature, notably as regards resacetophenone (Gregor, *Monatsh.*, 1894, **15**, 437, and Wechsler, *ibid.*, p. 239) and euxanthone (Graebe and Ebrard, *Ber.*, 1882, **15**, 1678), from which fully ethylated products have been obtained.

More recently it was shown (T., 1902, **81**, 206) that myricetin, an hydroxyquercetin, which without doubt contains an hydroxyl group adjacent to the carbonyl group, readily yields the hexaethyl derivative, and it was accordingly suspected that under suitable conditions a complete ethylation of other flavone colouring matters could also be effected. This proved to be the case, good yields of the fully ethylated derivatives of quercetin, luteolin, apigenin (P., 1912, **28**, 329), gossypetin (this vol., p. 654), and quercetagetin (*ibid.*, p. 209) being obtained by the employment of an excess of ethyl iodide and alkali.

On the other hand, with quercetagetin and gossypetin (*loc. cit.*) it was possible, employing a considerable excess of methyl iodide and alkali, to prepare their fully methylated derivatives, and this was regarded as remarkable because one at least of these compounds must contain an hydroxyl group adjacent to the carbonyl group. It accordingly suggested itself that as in the ethylation process, there was possibly no difficulty in fully methylating compounds of this type, the failures in the past being due to a non-employment of an excess of the reagents, although it was to be borne in mind that whereas in quercetagetin or gossypetin the hydroxyl group adjacent to the carbonyl group is present in a dihydroxyquinol nucleus, in quercetin and the better-known flavones the corresponding group in almost every case is phloroglucinol; thus luteolin (T., 1900, **77**, 1316), with excess of iodide and alkali, gives not only luteolin trimethyl ether, but methyl-luteolin trimethyl ether, a methyl group having entered the phloroglucinol nucleus, and this behaviour cannot be considered abnormal in view of the well-known properties of phloroglucinol itself under similar conditions. It was accordingly probable that other flavones containing this group would behave similarly rather than yield a compound of the usual type, although remarkably enough only luteolin and the closely allied genistein (*ibid.*, p. 1310) have hitherto been found to give an abnormal result in this respect.

In order to decide this point a study of the methylation of

quercetin, the most readily accessible of all natural yellow colouring matters, has been carried out.

For the preparation of quercetin, commercial flavin, the yellow variety, an extract of quercitron bark, which consists of impure quercitrin, was chiefly employed.* Two hundred grams of the material were exhausted with 1500 c.c. of boiling alcohol, leaving 14 grams of an insoluble, brown powder, the clear liquid being concentrated to 700 c.c. and diluted with 500 c.c. of boiling water. The crystals which were deposited on keeping for several hours were cautiously washed with small amounts of alcohol of increasing dilution, and when dry weighed 145 grams. This product consisted of almost chemically pure quercitrin, and when hydrolysed with boiling 2 per cent. sulphuric acid (20 grams in 1500 c.c.) gave practically a theoretical yield of quercetin.

Twenty grams of quercetin in 220 c.c. of methyl alcohol and 120 c.c. of methyl iodide were boiled with a solution of 40 grams of potassium hydroxide in 150 c.c. of methyl alcohol, 5 c.c. at a time during two days. The yellow, creamy mass of potassium quercetin at first formed gradually disappeared; after about six hours a clear liquid usually resulted, and at the close of the operation the addition of fresh alkali gave little or no colour change. After removal of unattacked methyl iodide and the greater portion of the alcohol by distillation, the residue was diluted with water, the mixture extracted with ether, and the ethereal solution washed with dilute alkali, the aqueous liquid and alkaline washings (A) being reserved for examination. On concentrating the ether, crystals gradually separated; these were collected, crystallised twice from acetone, and repeatedly from pyridine until a constant melting point was obtained. The yield of pure substance was approximately 1 gram.

Found: C=65.10; H=5.98; CH₃=19.30.

C₂₁H₂₂O₇ requires C=65.28; H=5.70; CH₃=19.43 per cent.

This compound melts at 213–215°, is insoluble in alkali, gives no colour change with alcoholic potassium hydroxide, and is evidently completely methylated. It is distinguished by its sparing solubility in ordinary solvents.

The ethereal mother liquor on evaporation gave a yellow, crystalline residue, which was a mixture of substances. By a fractional crystallisation from alcohol, discarding the more insoluble portion, the main product was isolated as yellow prisms (1.5 grams), which sintered at 170° and melted at 176–178°. Suspecting that it was still impure, it was acetylated with boiling acetic anhydride, an

* Quercetin from rutin has also been employed for one experiment with results similar to those given by the quercitron bark preparation.

operation which could not be safely accomplished under three hours. Addition of alcohol caused the separation of colourless needles, which by crystallisation first from acetone and finally from acetic acid melted at 178—180°.

Found: $\text{CH}_3 = 14.38$.

$\text{C}_{20}\text{H}_{19}\text{O}_7(\text{C}_2\text{H}_3\text{O})$ requires $\text{CH}_3 = 14.49$ per cent.

The acetyl derivative was now hydrolysed with boiling dilute alcoholic potassium hydroxide, and the product was isolated, by dilution with water and acidification, as pale yellow needles melting at 184—185°.

Found: $\text{C} = 64.40$; $\text{H} = 5.42$; $\text{CH}_3 = 16.31$.

$\text{C}_{15}\text{H}_5\text{O}_3(\text{CH}_3)(\text{O}\cdot\text{CH}_3)_4$ requires $\text{C} = 64.51$; $\text{H} = 5.38$;
 $\text{CH}_3 = 16.13$ per cent.

This substance resembles quercetin tetramethyl ether (m. p. 156—157°), but differs from it in melting point and by its more sparing solubility in solvents. With 80 per cent. alcoholic potassium hydroxide it yields a bright yellow potassium salt crystallising in needles, and this is decomposed by water with separation of the original compound.

In order to study the hydrolysis of this compound, 0.87 gram was digested with a boiling solution of 1.8 grams of potassium hydroxide in 9 c.c. of 80 per cent. alcohol for several hours, but as little action had thus occurred, the mixture was heated in a sealed tube to 185° for two and a-half hours. The product was evaporated to dryness, the residue dissolved in water, and the solution treated with carbon dioxide, which then gave to ether a small amount of a colourless, viscid, phenolic substance, readily soluble in the usual solvents. In order to identify this compound it was dissolved in dilute sodium carbonate, the solution treated with benzenediazonium sulphate, and the red precipitate of the azobenzene compound, collected, and crystallised from alcohol. It separated as a spongy mass of orange-red needles, melting at 199—201°, and was recognised as identical with the compound obtained in a similar way from the phenolic product of the hydrolysis of methyl-luteolin trimethyl ether (*loc. cit.*), which, with little doubt, is bisbenzeneazomethylphloroglucinol monomethyl ether. The acid product of the hydrolysis isolated in the usual manner melted at 180—182°, and consisted of veratric acid.

Evidently, therefore, this product of the methylation of quercetin which melts at 184—185° is *methylquercetin tetramethyl ether*, and it is accordingly evident that quercetin and luteolin exhibit a similar behaviour when methylated with an excess of methyl iodide and alkali, in that a methyl enters the phloro-

glucinol nucleus of both compounds. The composition and properties of the more sparingly soluble substance, $C_{21}H_{22}O_7$, melting at $213-215^\circ$, are in agreement with the suggestion that it is the further methylation product of the compound melting at $184-185^\circ$, and is in reality *methylquercetin pentamethyl ether*.

In order to determine if this compound when hydrolysed gives products analogous to those obtained from quercetin pentamethyl ether, which on this assumption should be the case, 0.4 gram was digested with a boiling solution of 2 grams of potassium hydroxide in 80 per cent. alcohol for six hours. After removal of the alcohol the residue was dissolved in a little water, and treated with carbon dioxide, which caused the separation of a colourless, crystalline precipitate; this crystallised from alcohol in fine needles, melting at $148-149^\circ$; and in appearance and general properties resembled the methoxyfisetol dimethyl ether, melting at $102-104^\circ$, which Herzig (*Ber.*, 1909, **42**, 155) obtained in a similar way from quercetin pentamethyl ether. It is, however, somewhat more sparingly soluble than the latter in solvents, and is to be regarded as *methoxymethylfisetol dimethyl ether*. The acid product of the hydrolysis melted at $180-182^\circ$, and consisted of veratric acid. Little doubt can be therefore entertained that the constitution above suggested for the compound $C_{21}H_{22}O_7$ is correct.

By demethylation with hydriodic acid both the tetra- and pentamethyl ethers should give methylquercetin, and this is probably the case. The products obtained in this manner crystallised from dilute alcohol in pale yellow needles, and as was to be anticipated closely resembled quercetin itself, but the amount of substance available was not considered to be sufficient for an accurate comparison of the two substances.

The final mother liquors obtained during the purification of the methylquercetin tetramethyl ether yielded a small amount of quercetin tetramethyl ether, which was identified by its melting point and general properties.

The products, soluble in ether, of the methylation above described, averaged merely 15 per cent. by weight of the quercetin originally employed, and it accordingly became evident that a considerable amount of substance must have been retained in solution by the aqueous liquid (4).

Although after remaining for several days it was observed in one experiment that the solution had deposited a small amount of crystalline matter; in other cases this remained almost perfectly clear for long periods. By saturation with salt, however, a voluminous, curdy precipitate separated, which on keeping somewhat increased in quantity, and this was collected, washed with salt

solution, and thoroughly drained on a porous tile. By crystallisation from acetone it was obtained in colourless needles, melting at 150—151°. The yield averaged 10 grams.

Found: C=64.43; H=5.72; $\text{CH}_3=20.07$.

$\text{C}_{15}\text{H}_5\text{O}_2(\text{O}\cdot\text{CH}_3)_5$ requires C=64.51; H=5.38;

$\text{CH}_3=20.16$ per cent.

It evidently consisted of quercetin pentamethyl ether, and full proof as to its identity was obtained by an examination of the products of its hydrolysis with alcoholic potassium hydroxide, which, as anticipated, proved to consist of veratric acid and the methoxyfisetol dimethyl ether melting at 102—103°.

There is accordingly no difficulty in obtaining from quercetin by means of methyl iodide and alkali considerable amounts of its fully methylated derivative, and it is evident that the presence of the phloroglucinol nucleus does not affect this reaction beyond exerting a tendency to cause the formation of a trifling quantity of the corresponding methyl compound. It is indeed probable that quercetin pentamethyl ether is in reality formed when much smaller amounts of the reagents are employed, but that the peculiar property it possesses of remaining dissolved, probably as a colloid when the methylation product is treated with much water, has escaped the attention of previous workers. Again, Herzig (*loc. cit.*), who prepared this substance with methyl sulphate by the ordinary method, obtained a yield of only 25 per cent., owing, no doubt, to this cause. Possibly a failure to isolate the corresponding derivative of such other flavones, as chrysin, apigenin, and luteolin, is similarly to be accounted for, because there can now be no reason to infer that fully methylated compounds cannot be prepared by this method owing to the presence of an hydroxyl group adjacent to the carbonyl group. Indeed, during the preparation of apigenin dimethyl ether (T., 1900, **77**, 416) the presence of a second compound insoluble in alkali, probably apigenin trimethyl ether, was detected. Further experiments on the methylation of these and other hydroxyketonic compounds will be carried out as soon as opportunity occurs.

An account of a study of the ethylation products of quercetin, apigenin and luteolin has been already described (P., 1912, **28**, 329), although details of the procedure employed have not previously been given. This, it may here be pointed out, was practically identical with that found serviceable for the methylation of quercetin, 5 grams of the substance in 60 c.c. of alcohol and 30 c.c. of ethyl iodide being treated at the boiling temperature with a solution of 10 grams of potassium hydroxide in alcohol during two days, a gradual addition of the alkali being adopted to avoid

hydrolysis of the ethylated product which occurs to some extent when this reagent is added all at once. The ethylated compounds are soluble in ether, and can thus be readily isolated.

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CLXXIX.—*The Absorption Spectra of Various Derivatives of Aniline, Phenol, and Benzaldehyde.*

By JOHN EDWARD PURVIS.

In a previous communication (T., 1910, **97**, 1546) the author has shown that in the ultra-violet regions the vapour of aniline has a considerable number of fine bands in the region between λ 3005 and λ 2430, and that there is also a wide band between about λ 2400 and λ 2320 which was not resolved into finer bands, whereas the homologues of aniline possess no such series of fine bands, the vapour bands and the solution bands of the latter being then comparable except in position. It has also been shown by the author (T., 1911, **99**, 811, 1699, 2318) that whereas neither the vapours nor the alcoholic solutions nor very thin films of the iodo-derivatives of benzene and toluene show any series of fine bands, the corresponding chloro- and bromo-compounds have a well-marked series of fine bands. It has further been proved (Purvis and McClelland, this vol., p. 1088) that the vapours of phenol, the cresols, the monochlorophenols, the monochloroanilines and benzaldehyde show a considerable number of fine bands, whereas the vapours of the nitro-derivatives of these substances show no such bands, the large solution bands and the vapour bands then being similar in general appearance.

It seemed to be desirable to continue the investigation of the bromo-, the iodo-, and the amino-derivatives of some of the latter compounds to see (1) how far the absorption is affected by the substitution of bromine and iodine in place of chlorine; (2) how far it is affected by the addition of additional chlorine or bromine atoms; (3) how far the absorption of the neutral solutions of the aniline compounds is affected by the addition of acid; and (4) how far the absorption is affected in such substances as aminophenol and aminobenzaldehyde when compared with aniline, phenol, and benzaldehyde.

The following substances were examined: *o*-, *m*-, and *p*-bromo-

anilines; *o*-, *m*-, and *p*-iodoanilines; 2:4-dichloroaniline; *p*-bromophenol; *p*-iodophenol; 2:4:6-trichlorophenol; 2:4:6-tribromophenol; *m*-aminophenol; *m*-dimethylaminophenol; *p*-aminobenzaldehyde, and *p*-dimethylaminobenzaldehyde.

The apparatus and method of experiment have been described before.

Solutions.

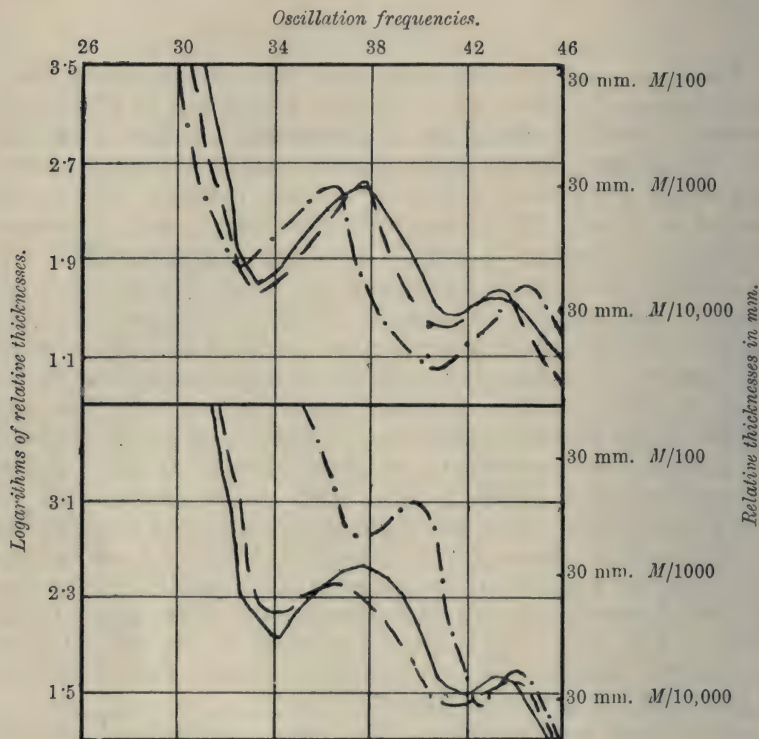
The *o*-, *m*-, and *p*-chloroanilines have been investigated by Baly and Ewbank (T., 1905, **87**, 1355), and they found in a *M*/1000-neutral alcoholic solution of *o*-chloroaniline a large band at $1/\lambda$ 3450 (λ 2900), in the *m*-compound a band at $1/\lambda$ 3410 (λ 2930) and in the *p*-compound a band at $1/\lambda$ 3360 (λ 2980). The curves also show that in the *o*-compound there was a rapid extension of the rays between $1/\lambda$ 4000 (λ 2498) and $1/\lambda$ 4200 (λ 2380) at 3 to 5 mm. thickness of the solution, and in the *p*-compound there was a rapid extension between $1/\lambda$ 3900 (λ 2563) and $1/\lambda$ 4400 (λ 2270). There can be no doubt that the latter phenomena mean the presence of another band, for on investigating *M*/10,000-solutions of the *o*-, *m*-, and *p*-chloroanilines the extensions of the rays noticed in the *M*/1000-solutions open out into weak bands, the head of which in the *o*-compound is at about $1/\lambda$ 4200 (λ 2380), in the *m*-compound at $1/\lambda$ 4200 (λ 2380), and in the *p*-compound at $1/\lambda$ 4170 (λ 2390). Baly and Ewbank (*loc. cit.*) also showed that strongly acid solutions of these isomerides influenced the appearance and the position of the less refrangible band they describe. It should also be recalled that Hartley and Huntingdon (*Phil. Trans.*, 1879, **170**, I., 257) found two bands in alcoholic solutions of aniline, namely, one at λ 285— λ 274, and the second at λ 240— λ 232 at greater dilutions.

o-, *m*-, and *p*-Bromoanilines.—In neutral solutions of each of these substances there are two bands (Fig. 1, upper curves), a strong, less refrangible one, and a more refrangible weaker band. The curves of the *o*- and *m*-compounds are not unlike, although there is a slight shift of the *m*-compound towards the red end; and in the *p*-compound the shift is much greater. Also the less refrangible band of the *p*-compound is not quite so strong as that of the *o*- and *m*-compounds, whereas the more refrangible band is stronger than the corresponding band of the *o*- and *m*-compounds. It is also to be noticed that the two bands are comparable with the two of aniline and of the *o*-, *m*-, and *p*-chloroanilines, except in position. The solutions were also investigated in the presence of slight excess of acid (Fig. 1, lower curve), and it will be seen that there is a slight shift of the absorption towards the more refrangible side,

which is more marked in the *p*-compound than in the other isomerides. The bands are also considerably reduced in intensity and persistency; and, again, this is most marked in the *p*-compound.

o-, *m*-, and *p*-Iodoanilines.—Neutral solutions (Fig. 2, upper

FIG. 1.



Upper curves.

Neutral solutions { *o*-Bromoaniline (continuous).
 m-Bromoaniline (dash).
 p-Bromoaniline (dot and dash).

Lower curves.

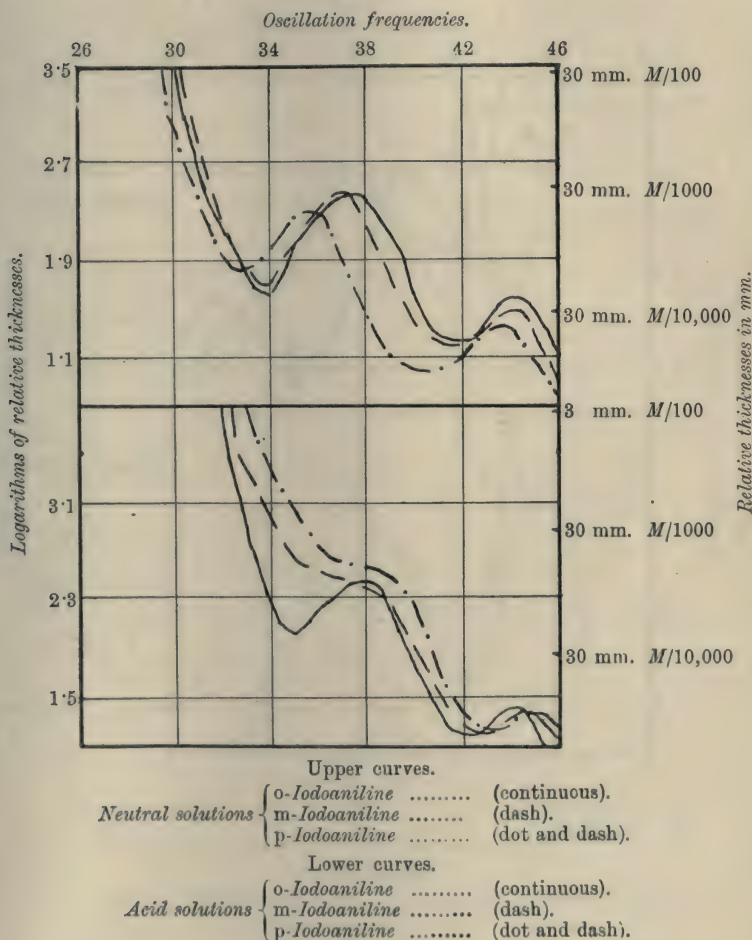
Acid solutions { *o*-Bromoaniline (continuous).
 m-Bromoaniline (dash).
 p-Bromoaniline (dot and dash).

curves) of these substances give similar results to the corresponding bromine compounds, except that the less refrangible band is not quite so strongly marked, whereas the more refrangible band appears to be stronger. In slightly acid solutions (Fig. 2, lower curves) there is again a shift towards the more refrangible regions

in all these substances; and there is a considerable diminution in the intensity of the bands.

2:4-Dichloroaniline.—Both the neutral and the acid solutions of the substance show two bands (Fig. 3, upper curves III and IV), and it will be noticed that the more refrangible band comes out

FIG. 2.



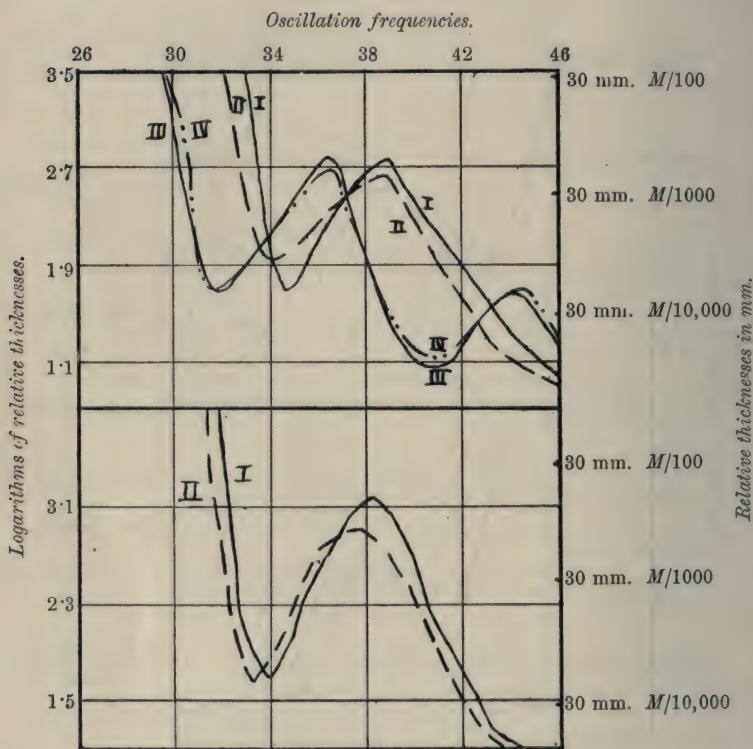
quite strongly. The curve of the acid solution does not show any very marked difference; and the original photographs are quite definite in this direction.

p-Bromophenol and p-Iodophenol.—The absorption curve (Fig. 3, upper curves I and II) shows one strong band in each substance,

which is similar to the band found in *p*-chlorophenol (*loc. cit.*). The band of the iodo-compound is shifted more towards the red end, and it is not quite so strong as that of the bromine compound.

2:4:6-Trichlorophenol and 2:4:6-Tribromophenol.—Each sub-

FIG. 3.



Upper curves.

- | | |
|---------------------------|-------------------------------------|
| I. <i>p</i> -Bromophenol. | III. 2:4-Dichloroaniline (neutral). |
| II. <i>p</i> -Iodophenol. | IV. „ (acid). |

Lower curves.

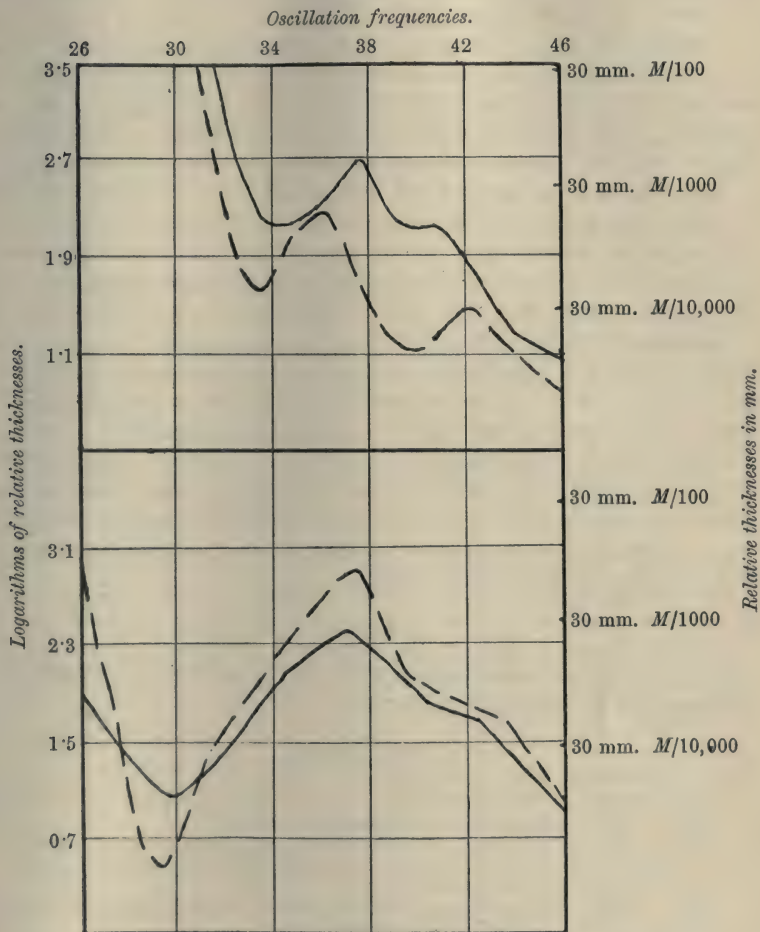
- | | |
|---------------------------|---------------------------|
| I. 2:4:6-Trichlorophenol. | II. 2:4:6-Tribromophenol. |
|---------------------------|---------------------------|

stance has one strong band (Fig. 3, lower curves), which is not unlike that of phenol and the other halogen derivatives of phenol. It differs chiefly in position from these.

m-Aminophenol and *m*-Dimethylaminophenol.—The instability of the former compound in solution was not favourable to a very exact study of its absorption. There was, however, a fairly strong

band at $1/\lambda$ 3440; but a more refrangible band indicated at about $1/\lambda$ 4000 was indefinite (Fig. 4, upper curves). The *m*-dimethyl

FIG. 4.



Upper curves.

m-Aminophenol (continuous).

m-Dimethylaminophenol (dash).

Lower curves.

p-Aminobenzaldehyde (continuous).

p-Dimethylaminobenzaldehyde (dash).

compound showed two well-marked bands at $1/\lambda$ 3390 and $1/\lambda$ 4000. *p*-Aminobenzaldehyde and *p*-Dimethylaminobenzaldehyde.—Each

of these compounds (Fig. 4, lower curves) shows a large band at $1/\lambda$ 3000 and $1/\lambda$ 2930 respectively, and there were also indications of a weaker band on the more refrangible sides, as indicated by the step-out of the transmitted rays at $1/\lambda$ 4100— $1/\lambda$ 4260 and $1/\lambda$ 3950— $1/\lambda$ 4350 respectively.

Results of the Solutions.—The preceding observations show (1) that the absorption bands in the mono-halogen derivatives of aniline are comparable with those of the base itself except in position; and that the addition of acid produces a shift of the bands and the general absorption towards the more refrangible regions, as well as reduces the intensities very considerably; and on the other hand, the addition of acid to the solution of 2:4-dichloroaniline causes little or no change in the latter direction; (2) that in the halogen derivatives of phenol the single band of the substance remains very like that of phenol itself, and differs chiefly in position; (3) that in each of the aminophenols there are two bands which are not unlike the aniline bands except in position; (4) that in each of the aminobenzaldehydes there is one large strong band which crosses the region of the less refrangible bands of aniline and of benzaldehyde, and extends into the regions of the visible spectrum; and there is also a doubtful weak band on the more refrangible side, which is comparable in position with the more refrangible weak band of aniline, as well as with the band of benzaldehyde in the same region.

Vapours.

The vapours were enclosed in a 200 mm. tube and investigated at various temperatures and pressures.

o-Bromoaniline.

t°	Pressure in mm.	
45	829	The rays were transmitted to λ 2140.
60	859	There were three very weak and diffuse bands at λ 2909, λ 2987, and λ 2290; and the rays were then transmitted to about λ 2380.
70	889	The rays were absorbed between λ 3040— λ 2760 and then transmitted to about λ 2530.
90	919	The rays were absorbed from λ 3050, but the strong Cd line at λ 2573 was just visible.

The rapid extension of the rays between 45° and 60° , that is, between λ 2380 and λ 2140, represents the weak solution band found in this region; there is no resolution of this band into a series of fine bands, and the number of bands in the less refrangible region at 60° and 70° is considerably reduced as compared with the aniline and *o*-chloroaniline vapours (*loc. cit.*). An examination of the plates of *o*-chloroaniline also shows a rapid extension of the

rays in this region of the vapours between λ 2140 at 30° and λ 2460 at 45° , but no fine bands were visible.

m-Bromoaniline.—At 60° and 854 mm. the following bands were observed :

λ .	
2962	These bands were very narrow and faint ; they compare fairly well with those of aniline and <i>m</i> -chloroaniline (<i>loc. cit.</i>) ; but there is a slight shift of about 5 units towards the red end as compared with those of the vapour of <i>m</i> -chloroaniline, and of about 35 units as compared with those of aniline. The more refrangible bands of aniline and of <i>m</i> -chloroaniline entirely disappear.
2958	
2954	
2935	
2933	
2912	
2898	

The rays were then transmitted to about λ 2190.

At 75° and 884 mm.

λ .	λ .
2980 w.	2902 v.w.
2962 w.	2898 w.
2958 v.w.	2892 v.w.
2954 mod. str.	
2950 w.	The rays were then
2935 v.w.	feebly absorbed to
2933 w.	λ 2760 and then
2914 v.w.	transmitted to
2905 „	λ 2420.

At 90° and 914 mm.

The rays were absorbed between λ 2990— λ 2770 and then transmitted to λ 2560.

At 100° and 930 mm.

The rays were absorbed between λ 3030— λ 2730 and then transmitted to λ 2570.

The rapid extension of the rays between λ 2450 at 75° and λ 2190 at 60° corresponds with the weak band found in this region in the solution, and there is no appearance of any finer bands. A similar rapid step-out of the rays occurs in the vapour of *m*-chloroaniline between λ 2470 at 60° and λ 2150 at 45° (*loc. cit.*) ; and also the number of bands in *m*-bromoaniline vapour is considerably reduced as compared with *m*-chloroaniline.

p-Bromoaniline.—At 75° and 894 mm. the rays were weak between λ 2480 and λ 2330, and then transmitted fairly strongly to λ 2120.

At 90° and 924 mm.

λ .
3072 diff.
3046 mod. str., diff.
3040 „ „
3031 v.w.
3025 „
3020 mod. str.
3012 „
3006 w.
2996 mod. w., diff.
2992 „ „
2989 „ „

The rays were then feebly absorbed to about λ 2780 and then transmitted to λ 2530.

At 100° and 940 mm.

λ .
3080 to 3072 w., diff.
3052 „ 3044 mod. str., diff.
3022 „ 3012 „ „
3000 w.
2996 mod. w.

The rays were then absorbed to λ 2780 and then transmitted to λ 2630.

The rapid step-out of the rays between λ 2530 at 90° and λ 2150 at 75° corresponds with the weak solution band. In the vapour of *p*-chloroaniline (*loc. cit.*) also there is a rapid extension of the rays from λ 2550 at 75° to λ 2140 at 60° . Also the bands in the vapour of *p*-bromoaniline are not unlike those of *p*-chloroaniline, except that there is a slight shift of the former of about 5 units towards the red end.

o-Iodoaniline.

t° .	Pressure in mm.	
45	829	The rays were transmitted to about λ 2150.
60	859	The rays were weakly absorbed between about λ 3030— λ 2800 and then transmitted to λ 2430, but the Cd lines 2329 to 2194 were visible.
75	889	The rays were absorbed between λ 3080— λ 2780 and then transmitted to about λ 2480.
90	919	The rays were absorbed from about λ 3100, but the strong Cd lines 2748 and 2573 were just visible.

m-Iodoaniline.

75	889	The rays were transmitted to about λ 2200.
90	919	„ „ feebly absorbed between λ 3000— λ 2820 and then transmitted to about λ 2430; the two Cd lines 2321 and 2313 were just visible.
100	925	The rays were absorbed between λ 3040— λ 2800 and then transmitted to λ 2480.

p-Iodoaniline.

60	866	The rays were transmitted to about λ 2140.
75	896	„ „ „ „ „ „ λ 2510, but the series of Cd lines 2329 to 2144 were strongly marked.
90	926	The rays were a little weak between λ 3040— λ 2800, and then transmitted to λ 2570.
100	942	The rays were fairly well absorbed between λ 3080— λ 2780 and then transmitted to λ 2650.

The outstanding results of the vapours of the three iodoanilines are: (1) the complete absence of all the fine bands found in the vapours of aniline and in the *o*-, *m*-, and *p*-chloro- and bromoanilines; and (2) the well-defined appearance of the second band in the more refrangible regions between λ 2510 and λ 2339, which band is not unlike that in the corresponding chloro- and bromo-compounds as well as in aniline, and it is better marked in the para-compounds than in the ortho- and meta-compounds.

2:4-Dichloroaniline.

<i>t</i> °.	Pressure in mm.	
45	836	The rays were transmitted to about λ 2120
60	866	" " weak between λ 2480 to the Cd line λ 2329 and then transmitted to λ 2140.
75	896	The rays were fairly well absorbed between λ 3120— λ 2800 and then transmitted to λ 2550.
90	926	The rays were absorbed between λ 3140— λ 2800 and then transmitted to λ 2630.
100	942	The rays were absorbed from λ 3200, but there was a feeble transmission between the Cd line λ 2748 and about λ 2680.

Dichloroaniline vapour thus shows no series of fine bands like the *o*-, *m*-, and *p*-chloroanilines. There are two bands, a strong one between λ 3140 and λ 2800, and a weaker one between λ 2480 and λ 2329, and both of which correspond with the two solution bands.

p-Bromophenol.

Abbreviations: w.=weak; diff.=diffuse; mod.w.=moderately weak; mod.str.=moderately strong; v.w.=very weak.

At 75° and 896 mm.

λ .	
2926 to 2922 w., diff.	
2912 " 2910 "	
A	{ 2908 w.
	{ 2903 w.
	{ 2900 w.
	{ 2899 mod. w.
B	{ 2896 " str.
	{ 2890 v.w.
	{ 2887 " "
	{ 2883 " "
C	{ 2880 mod. w.
	{ 2878 " "
	{ 2873 mod. str.
	{ 2871 str.
D	{ 2869 mod. w.
	{ 2865 " "
	{ 2863 " "
	{ 2858 w.
E	{ 2855 mod. w.
	{ 2854 " "
	{ 2850 mod. str.
	{ 2846 " "
F	{ 2842 v.w.
	{ 2841 " "
	{ 2838 mod. w.
	{ 2836 " "
	{ 2833 " "
	{ 2829 " "
	{ 2820 w., diff.
	{ 2814 " "
	{ 2812 mod. str.
	{ 2809 " "
	2806 to 2804 mod. w.

At 90° and 926 mm.

λ .	
2928 to 2921 w., diff.	
2913 " 2909 "	
A	{ 2907 wide band, sharper
	{ to on the more re-
	{ 2897 frangible edge.
B 2891 to 2884 v.w. and diff.	
C	{ 2881 str., wide, sharp on
	{ to more refrangible
	{ 2872 edge.
	{ 2869 w., diff.
	{ 2864 " "
D	{ 2863 str., wide, sharper
	{ to on more refrangible
	{ 2847 edge.
	2843
	2841
E 2839 to 2828 w.	
F 2822 to 2809 w.	

p-Bromophenol (continued).

At 75° and 896 mm.

	λ .
G	2800 w.
	2798 mod. w.
	2796 mod. str.
	2793 „
	2792 sur.
	2790 mod. w.
H	2788 „
	2780 w., diff.
	2777 „
	2763 „
	2735 v.w.
	2734 „
	2718 „
	2715 „
	2708 v.w.
	2705 „
	2700 „

The rays were then transmitted to
about λ 2820; 50 bands.

At 90° and 926 mm.

	λ .
G	2803 to 2790 w., diff.
H	2782 w., diff.
	2779 „
	2774 to 2767 v.w.
	2734 v.w.
	2731 „
	2718 „
	2715 „

The rays were then transmitted to
about λ 2470; 20 bands.

At 100° and 942 mm. pressure there was a weak diffuse band from λ 2930 to λ 2922, and another between λ 2911 and λ 2897; from here the rays were absorbed to λ 2710, and then transmitted to λ 2530. At the increased temperatures and pressures, therefore, the finer bands widen into each other, so that one strong band is produced which is not unlike the solution band.

The more marked features of the vapour of *p*-bromophenol are (1) the large number of fine bands which can be arranged in groups; the principal groups are marked A, B, C, D, E, F, G; (2) the production of one single band at the higher temperatures and pressures, which is similar to the solution band.

The vapour bands of *p*-bromophenol are very like those of the vapour of *p*-chlorophenol (*loc. cit.*), which have been re-measured, except that the former are shifted more towards the red end, and a number of the more refrangible bands have disappeared. The heads of the stronger bands in the vapours of the two substances are compared in the following table, which shows the differences in the shift.

p-Bromophenol.

	λ .
A	2896
B	2883
C	2871
D	2846
E	2829
F	2809
G	2788

p-Chlorophenol.

	λ .
	2892
	2881
	2869
	2841
	2824
	2807
	2785

p-Iodophenol.

<i>t</i> °.	Pressure in mm.	
75	884	The rays were transmitted to about λ 2150.
90	914	„ „ weak between about λ 2880— λ 2750 and then transmitted to about λ 2350.
100	930	The rays were well absorbed between λ 2920— λ 2720 and then transmitted to about λ 2380.

The striking result of the vapour of *p*-iodophenol proves that all the finer bands of phenol (*loc. cit.*), of *p*-chlorophenol, and *p*-bromophenol have completely disappeared, and the one large band is comparable with the solution band.

2:4:6-Trichlorophenol.

<i>t</i> °.	Pressure in mm.	
75	894	The rays were moderately well absorbed between λ 2948—2936, between λ 2913— λ 2909, feebly between λ 2854— λ 2841, and then absorbed between λ 2833— λ 2800. After this they were transmitted to λ 2260.
90	924	The rays were absorbed between λ 3000— λ 2790 and then transmitted to λ 2380.
100	940	The rays were absorbed between λ 3030— λ 2730 and then transmitted to λ 2450.

2:4:6-Tribromophenol.

<i>t</i> °.	Pressure in mm.	
90	924	The diffuse bands found at 75° in trichlorophenol were not very well marked; there were traces of bands between λ 2950— λ 2936 and λ 2914— λ 2910; the rays were then feebly absorbed to about λ 2820. Afterwards they were transmitted to λ 2270.
100	940	The rays were feebly absorbed between λ 2980— λ 2830 and then transmitted to λ 2300.

The experiments show, therefore, that the vapour bands found in phenol and in the chloro- and bromo-phenols have been almost obliterated in the trisubstituted compounds. Also it should be noted that, at the higher temperatures and pressures, the absorption band is similar to the solution band, except in position.

p-Aminobenzaldehyde.—At 60° and 860 mm. pressure the following bands were observed and measured:

λ .
{ 3027 w.
{ 3017 mod. str.
{ 3003 v. w.
{ 3000 w.
{ 2998 w.
{ 2993 mod. str.
{ 2964 w.
{ 2957 mod. str.
{ 2954 w.
{ 2950 mod. str.

λ .
{ 2930 v. w.
{ 2927 w.
{ 2923 mod. str.
{ 2918 " "
{ 2895 v. w.
{ 2890 " "
{ 2886 w.

The rays were then feebly absorbed to λ 2790, and transmitted to λ 2450; but beyond this the series of Cd lines 2329 to 2144 were well marked.

t° .	Pressure in mm.	
75	890	The bands were similar to those at 60° ; the rays were more strongly absorbed from about λ 2886— λ 2790 and then transmitted to λ 2480.
90	920	The rays were absorbed between λ 3031— λ 3018, λ 3007— λ 2994; they were also absorbed from about λ 2970— λ 2780; and then transmitted to λ 2560.
100	936	The rays were absorbed from about λ 3050.

p-Dimethylaminobenzaldehyde.

t° .	Pressure in mm.	
90	920	The rays were absorbed between λ 3130— λ 2800 and then transmitted to about λ 2150.
100	936	The rays were absorbed between λ 3170— λ 2750 and then transmitted to λ 2270.

The results furnished by these aminobenzaldehydes show that the large number of fine bands found in aniline and in benzaldehyde (*loc. cit.*) has been greatly diminished in *p*-aminobenzaldehyde, and they have completely disappeared in the dimethyl compound. Also that at the higher temperatures and pressures the single vapour band of *p*-aminobenzaldehyde corresponds with the solution band. It is of some importance to recall that the fine bands found in the vapour of aniline completely disappear in the vapour of dimethylaniline and in other homologues of aniline (*loc. cit.*).

m-Aminophenol.—The completely dried substance was heated in the absorption tube above its melting point (122 — 123°). Just below the melting point the rays were transmitted to λ 2180. A few degrees above the melting point bands were observed at λ 2942, λ 2937, λ 2933, and λ 2926; they were very weak and difficult to measure; the rays were then feebly absorbed to about λ 2775, and afterwards transmitted to λ 2450. At five to ten degrees higher the same bands came out a little stronger, and the rays were also well absorbed to λ 2764 and then transmitted to λ 2510.

m-Dimethylaminophenol.

t° .	Pressure in mm.	
90	922	The rays were feebly absorbed between λ 2950— λ 2770, completely absorbed between λ 2550— λ 2330, and then transmitted to λ 2250.
100	938	The rays were moderately well absorbed between λ 2980— λ 2760, completely absorbed between λ 2580— λ 2320, and then freely transmitted to λ 2270.

The results given by the two aminophenols show that again the large number of fine bands found in aniline and phenol (*loc. cit.*) has considerably diminished in *m*-aminophenol, and completely disappeared in the dimethyl compound. Also that the two vapour bands of the latter correspond with the two solution bands; and that at the higher temperatures and pressures there is a tendency for the vapour bands of *m*-aminophenol to coalesce into bands comparable with the solution bands.

Results of the Vapour.—The results of the preceding observations are: (1) that the number of vapour bands in the isomeric bromoanilines is considerably less than the vapour bands of the corresponding chloroanilines; and that the large band in the more refrangible regions is not resolved into a series of fine bands characteristic of the less refrangible band; such phenomena are similar to those noticed in the corresponding more refrangible bands of aniline and its monochloro-derivatives; (2) that no fine bands occur in the vapour of the iodo-derivatives of aniline or of the dichloro-aniline, and that the two large bands observed are comparable with the solution bands except in position; (3) that there is a series of fine bands in *p*-chloro- and *p*-bromo-phenol which are completely absent in *p*-iodophenol; (4) that the vapour bands of phenol have almost disappeared in the vapour of trichloro- and tribromophenols, and the bands are comparable with the solution bands; (5) that there are a few fine bands in *p*-aminobenzaldehyde, but they are considerably less than in the vapour of aniline or of benzaldehyde, and that in *p*-dimethylaminobenzaldehyde these finer bands completely disappear; (6) that in *m*-aminophenol there are also a few fine bands which completely disappear from the vapour of *m*-dimethylaminophenol, and the bands become comparable with the solution bands; (7) that where there are two bands in any of the substances examined the more refrangible band is not resolved into fine bands on its less refrangible edge in the manner characteristic of the less refrangible band; (8) that in all the substances examined where there are series of vapour bands these bands gradually disappear with increasing temperatures and pressures, and the large bands which take their place are quite comparable with the solution bands, but the damping effect of the

solvent causes a shift of the absorption more towards the red end of the spectrum.

Discussion of the Results.

In the solutions of the aniline derivatives it is clear that the presence of the amino-group and its orientation influences the vibrations very considerably; for the slightly acid solutions of each substance show marked differences from the neutral solutions. But that the final result does not depend entirely on this group follows from the further fact that there is little or no difference between the neutral and acid solutions of 2:4-dichloroaniline.

The presence or absence of the finer vapour bands also does not appear to depend intrinsically on any added group or groups of atoms; for although the finer bands of benzene disappear in the iodo- and nitro-compounds (*loc. cit.*) they also disappear in dichloroaniline as well as in the iodoanilines.

Similarly in the halogen derivatives of phenol the finer bands of the substance itself and those of the chloro- and bromo-derivatives disappear in the iodo-compounds, and almost disappear in the trichloro- and tribromo-compounds.

That the phenomena are not merely caused by each vibration centre acting independently of the other centres also follows from the greatly reduced numbers of bands found in the vapours of aminophenol and aminobenzaldehyde, whereas aniline, phenol, and benzaldehyde have each a much larger number of bands. In all instances, however, when the fine vapour bands are replaced by large strong bands, and this occurs also when vapours which give finer absorption bands are subjected to increased temperatures and pressure, the phenomena are comparable with the solution bands.

It is suggested that the final result of the vibrations which produce absorption depends on the interaction of different centres of oscillation, and that they are centres of electronic vibrations set in motion by the radiant energy of the source of light whereby there is selective absorption of a part of the energy. In the solutions the vibrations are also influenced by those of the solvent, and there is also the resistance caused by a frictional damping force. The suggestion has been applied to explain the phenomena observed in various saturated and unsaturated aldehydes and ketones (Purvis and McClelland, T., 1912, **101**, 1514, 1810; this vol., p. 433), and it may be possible to give a similar dynamic explanation of the results of these benzene derivatives.

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CLXXX.—*The Viscosity of Cellulose Nitrate Solutions.*

By FRANK BAKER.

ALTHOUGH during the last few years a considerable amount of work has been carried out on the relation between viscosity and chemical constitution and on the viscosity of liquid mixtures and solutions, little attention has in this respect been paid to the colloids.

This is the more surprising in view of the fact that the formation of highly viscous solutions appears to be characteristic of a large number of these substances; the probable cause of this neglect is that the majority of such solutions are unstable, and also that the substances themselves do not lend themselves to quantitative investigations, owing to their somewhat indefinite nature.

The nitric esters of cellulose present certain very definite advantages over the majority of colloids from the point of view of an investigation into the physical properties of their solutions. They are readily soluble in a number of organic solvents, thus enabling the influence of the solvent to be examined, and also avoiding the use, as a solvent, of water, which for physico-chemical purposes is sometimes unsatisfactory as it is liable, owing to its high degree of association, to give rise to abnormal results. Further, they can be, in the ungelatinised state, readily dehydrated, and, if properly stabilised, yield solutions which do not change in viscosity, at least during the few days required for an experiment (Piest, *Zeitsch. Schiess. Sprengstoffwesen*, 1910, **5**, 409).

The viscosity of a solution of a cellulose nitrate has, for a long time, been regarded as a criterion of its value for certain purposes. The published work on this subject is, however, limited in extent (Bruley, *Mem. Poudres et Salpêtres*, **8**, 111; Lehner, *Zeitsch. angew. Chem.*, 1906, **19**, 1583; Lunge, *ibid.*, 1906, **19**, 2051; Berl and Klaye, *Zeitsch. Schiess. Sprengstoffwesen*, 1907, **2**, 381; Berl, *ibid.*, 1909, **4**, 81; Piest, *ibid.*, 1910, **5**, 409; *Zeitsch. angew. Chem.*, 1913, **26**, 24; Schwarz, *Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 32), and consists almost entirely of comparisons between different nitrocelluloses made with solutions at the same concentration. These determinations were made simply with the view of comparing nitrocelluloses prepared in different ways and from different materials. In most cases, also, the viscometer used was not one capable of giving true viscosities.

As a result of a large number of experiments that have been carried out with liquid mixtures, there appears to be no doubt that even in the case of mixtures of unimolecular liquids, in which neither association nor dissociation can take place, the viscosities of

these mixtures cannot be calculated from the viscosities of their components by any simple rule. Dunstan (T., 1907, **91**, 83) has pointed out relationships between the shape of the curves obtained and the molecular weights of the components—relationships which fail to hold in cases when association or dissociation occurs.

From purely theoretical reasoning, Lees (*Phil. Mag.*, 1901, [vi], **1**, 128) developed three formulæ for the relation between composition and viscosity of liquid mixtures, but none of these agreed with the experimental results of Linebarger (*Amer. J. Sci.*, 1896, [iv], **2**, 331) or of Thorpe and Rodger, T., 1897, **71**, 360). He found, however, that an empirical formula $\eta^n = a\eta_1^n + (1-a)\eta_2^n$, where a is the proportion by volume of the first component, and η_1 and η_2 the respective viscosities of the pure liquids, whilst n is a constant for a given pair of liquids, gave results which agreed fairly well with those actually observed with a considerable number of mixtures, both of non-associated and associated liquids.

In a previous paper the author has pointed out that with mixtures of alcohols with anisole and phenetole, the mere change from methyl to ethyl alcohol is sufficient to alter the viscosity-concentration curve from one capable of being expressed by a formula of the above type to one incapable of being so expressed, and thus the above formula cannot be regarded as having any theoretical significance.

Lately the view has been expressed that fluidities, instead of viscosities, are additive (compare Bingham, this vol., p. 964), except in cases where association or dissociation interferes. Viscosities of mixtures calculated on this hypothesis are, in general, nearer the experimental values than those calculated on the basis of an addition law for viscosities, and it is conceivable that the former hypothesis might be absolutely correct if the volume of a mixture was exactly equal to the sum of the volumes of the components.

The above-mentioned work deals only with homogeneous mixtures, and it would appear highly probable that in the case of dispersoids totally different results might be obtained.

The relationship between the concentration and viscosity of liquids of this type has been studied from a purely theoretical point of view by Hatschek (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 301; 1911, **8**, 34). Such mixtures he considers as divided into two classes, suspensoids and emulsoids. For the first class he derives the formula $\eta = \eta_0(1 + 9/2f)$, where η is the viscosity of the "solvent," and f the ratio volume of disperse phase/total volume.

For emulsoids, the formula obtained is $\eta = \eta_0 \frac{2/f}{\sqrt[3]{f}-1}$, where f stands for the ratio total volume/volume of disperse phase.

Neither of these expressions can be regarded as expressing the relation between viscosity and concentration, as neither will account for the high viscosities observed with even dilute solutions of certain of the nitrocelluloses.

The object of the experiments described in the present paper was to establish a quantitative relation between the concentration and viscosity of solutions of cellulose nitrates, and, further, to examine the effect of varying the solvents employed.

EXPERIMENTAL.

The solutions were made up by weight in Jena-glass flasks of 50 or 100 c.c. capacity, closed with stoppers formed from a piece of glass rod or tube, and a short length of rubber tubing. By this means the amount of rubber in contact with the liquid was small, and this tubing was repeatedly extracted with acetone before use.

In preparing a solution, a flask was dried and weighed, together with its stopper. A quantity of the cellulose nitrate, dried for four hours at 60—70°, was rapidly placed in the flask, and the whole re-weighed. This temperature of drying was adopted, as at higher temperatures a decomposition of the cellulose nitrate, insufficient to be detected by ordinary methods, but having a marked influence on the viscosity, is liable to take place.

The solvent, 25 or 50 c.c., was then added from a pipette, and the flask and contents again weighed. The flask was then clamped to the stirrer-axle of a thermostat at room temperature, and the cellulose nitrate brought into solution by several hours' shaking. When no gelatinous mass was visible, the solution was allowed to settle in a dark place for two or more days, according to the viscosity of the solution.

In making up the solutions, no allowance was regarded as necessary for the amount of mineral matter or for unnitrated cellulose present in the cellulose nitrates. The proportion of such insoluble matter was, however, only small, and would naturally be a constant for each sample, while the amount would be insufficient to obscure in any way the relationships between the different varieties of cellulose nitrate examined.

Since the concentrations of nitrocellulose in the solutions examined were only small, rarely exceeding 2 per cent., the densities of these solutions differed very little from those of the pure solvents. It was therefore assumed that the density was a linear function of the cellulose nitrate concentration, and in each series the densities of the pure solvent and of one solution were determined, and those of the remaining solutions calculated.

The determination of the density of the pure solvents was carried out in a Sprengel tube of 25 c.c. capacity, that of the cellulose nitrate solutions in a Regnault bottle of 10 c.c. capacity.

The limited degree of accuracy attainable in these experiments did not require that the weighings should be corrected to vacuum standard, nor was the density of the air taken into account in calculating the results of the viscosity determinations.

The viscometers used in the determination of the viscosities of the cellulose nitrate solutions were of the usual Ostwald-Poiseuille type. As it was desired to obtain results with solutions the viscosities of which varied from 0.003 to 40 C.G.S. units, it was obvious that one viscometer was incapable of being used over the whole range. A series of instruments was therefore constructed so that the times to be measured would, in general, be more than 100 seconds and less than twenty minutes. This stipulation was desirable, not only for convenience in working, but also because the majority of the solvents employed were somewhat volatile at 25°.

The following were the dimensions of the viscometers employed:

Volume of upper bulb	3	- 4	c.c.
Length of capillary	12	- 15	cm.
Mean head of liquid	12	- 15	„
Diameter of capillary	0.04	- 0.2	„

These viscometers were compared with each other, using mono-, di-, and tri-acetin and also glycerol, the viscometers of the greatest time of flow being also standardised with water, for which the value $\eta = 0.00891$ at 25° was taken.

Thus, in a viscometer the time of flow of which for water was about 100 seconds, the viscosity of triacetin could conveniently be determined, and this liquid used to determine the constant of a viscometer of wider capillary. In this second viscometer the time of flow for diacetin could be ascertained, and, ultimately, it was possible to determine with a fair degree of accuracy, the constant for a viscometer of which the calculated time of flow for water was about 0.1 second. By this method of standardisation, not only was the measurement of short times avoided, but also the use of liquids of low viscosity in viscometers with capillaries of wide bore—a source of considerable error in certain cases—was dispensed with.

Occasionally the viscosity of a nitrocellulose solution was determined, using two different instruments, and it was found that the viscosities thus measured did not differ by more than 1 per cent.

Whilst this error appears to be of considerable magnitude, it may be noted, first, that it is the sum of several errors of experiment,

and secondly, that since the effect of even a small amount of cellulose nitrate in the viscosity of a solution is so great, a comparatively large error in the determination of a viscosity will have little influence on the final results.

The various samples of cellulose nitrates employed were manufactured at Ardeer, and were selected from products made for use in various explosives. Such samples possessed considerable advantages over any that could be prepared in the laboratory, as by this means it was possible to obtain large uniform samples of stable material. Consequently, no attempt was made to use nitrates corresponding with a definite degree of nitration (the so-called penta-, di-nitrates, etc.).

Three samples of cellulose nitrates were employed in the following work: (a) Blasting soluble nitrocellulose, as used for the manufacture of blasting gelatin; (b) highly soluble nitrocellulose, as used in ballistite; and (c) guncotton prepared for the manufacture of cordite. Sample (a) was manufactured from cotton cop bottoms, the remaining two from bleaching waste. All three samples had undergone the usual stabilisation process.

The following table gives the results of analysis of these three samples:

	Nitrogen. Per cent.	Ash. Per cent.	Solubility in ether-alcohol. Per cent.
(a) Blasting soluble nitrocellulose	11.85	0.30	100
(b) Highly soluble nitrocellulose	12.28	0.60	97.4
(c) Guncotton.....	12.98	0.30	9.6

The solvents employed were, in most cases, obtained from Kahlbaum, and were redistilled immediately before use. The acetone was taken from a consignment intended for the manufacture of cordite. This was redistilled through a Young's column, and boiled at a constant temperature. The esters were also purified by treatment with dilute sodium carbonate solution to remove all traces of free acid, which, in some cases, has a very marked effect on the viscosity of cellulose nitrates. After this treatment they were thoroughly washed and dried before distillation.

One of the substances used as a solvent has not previously been described. This compound, *ethyl o-tolyethylcarbamate* (tolyl-ethylurethane), $C_{12}H_{17}O_2N$, was prepared exactly as phenylmethylurethane (Gebhardt, *Ber.*, 1884, **17**, 3042) by the action of ethyl-*o*-toluidine on ethyl chloro-formate. By a similar process phenyl-ethylurethane was also prepared. Those two substances were obtained as colourless oils, darkening to some extent on exposure to light. They possessed characteristic ethereal odours, and boiled without decomposition at $249^{\circ}/760$ mm. and $257^{\circ}/755$ mm. respec-

tively, the tolyl compound possessing the higher boiling point. Both compounds readily dissolved the "soluble" varieties of nitrocellulose, but only the tolyl compound was used in the present investigation.

The results of the viscosity determinations are given in the following tables Nos. II—XXV.

In dealing with solutions in different solvents, it is obvious that the relative values of the viscosities at any definite percentage of cellulose nitrate will vary according to whether this percentage is calculated by weight or by volume, and it is necessary to consider which of the two methods is to be preferred.

If the fundamental definition of viscosity is examined, it is to be observed that neither the density nor the mass of the liquid comes into consideration, whilst again, in dealing with the flow of liquids through capillary tubes the volume and not the mass of liquid is of importance. In the case of solutions of cellulose nitrates, in which the influence of the solute on the viscosity is extremely great, it would certainly appear more logical to regard the volume concentration of the nitrocellulose as the main factor, the mass of the material occupying the space between the nitrocellulose particles being comparatively unimportant.

For these reasons the concentration of cellulose nitrate is expressed in grams per 100 c.c. of solution, since the density of nitrocellulose in solution is not known with sufficient exactness to allow the volume of nitrocellulose per 100 c.c. to be used.

The fourth column of the tables II—XXV gives the values of $\log(\eta \times 10^3)$, values which have been used in plotting the curves. These have been added, owing to the fact that the curves obtained by plotting η against the concentration would be unintelligible, as the numerical rate of increase of η with the concentration is small at first, and becomes very great at higher concentrations. By the use of logarithms of the viscosities, the curves become manageable. The factor 10^3 is introduced merely to avoid the use of negative characteristics.

The final column of certain of the tables contains the values of $\log \eta$ calculated from a formula:

$$\eta = \eta_0(1 + ac)^k \quad . \quad . \quad . \quad . \quad . \quad . \quad (I),$$

where η_0 is the viscosity of the solvent, a and k are constants, and c the concentration of cellulose nitrate. From these tables, it appears that this formula gives results for η which correspond fairly well with those obtained experimentally.

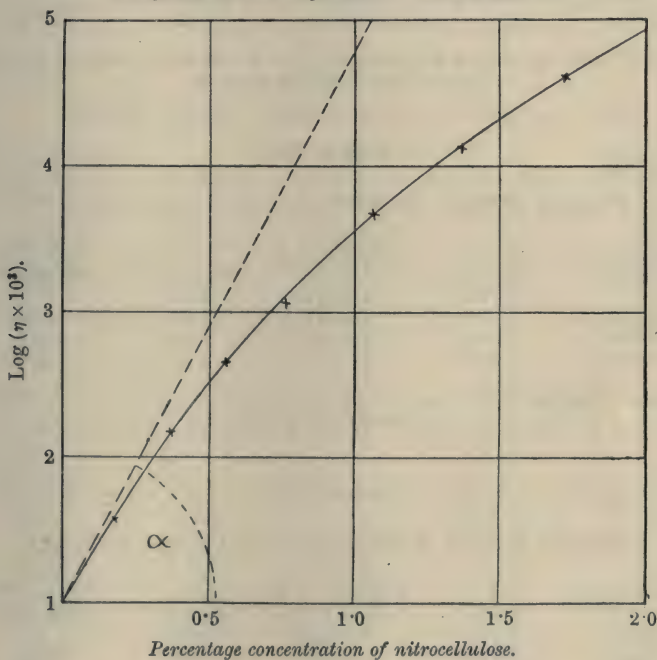
The separate values of a and k cannot, however, be calculated with great exactness, owing to the fact that k is comparatively large, and thus may vary considerably without greatly affecting the

figures obtained by calculation, provided, of course, that for each value of k the corresponding value of a is taken.

A somewhat better basis of comparison is afforded by taking the quantity ak as a characteristic function of each curve. This value can readily be obtained by drawing a tangent to the curve at its origin ($c=0$). Then we have from the above formula (1):

$$\left(\frac{d \log_e \eta}{dc}\right)_0 = ak,$$

Blasting soluble nitrocellulose in mixture of equal volumes of benzyl alcohol and ethyl ether. (Table XXIII.)



or, since the curves are drawn, using logarithms to base 10:

$$\frac{d \log_{10} \eta}{dc} = \frac{ak}{e},$$

and therefore $ak = 2.303 \tan \alpha$, where α is the angle between the tangent and the C axis.

All the curves obtained were of the same character, and therefore only one, that given by solutions of blasting soluble nitrocellulose in a mixture of equal parts of ethyl ether and benzyl alcohol, is shown.

TABLE II.

Blasting Soluble Nitrocellulose in Acetone at 25°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.	$\text{Log } \eta \times 10^3$ calculated.
0.0	0.7881	0.00315	0.498	—
0.2212	0.7895	0.01223	1.087	1.100
0.5261	0.7915	0.0590	1.771	1.771
0.7922	0.7940	0.176	2.246	2.250
1.058	0.7956	0.455	2.658	2.666
1.640	0.7995	2.240	3.350	3.408
2.348	0.8040	15.90	4.200	4.115
3.865	0.8140	168.0	5.226	(5.226)

The figures in the last column are calculated from the formula $\eta = \eta_0(1 + 1.024 \times c)^{6.8}$;
 ak calculated from curve = 6.22.

TABLE III.

Blasting Soluble Nitrocellulose in Acetone at 15°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.	$\text{Log } \eta \times 10^3$ calculated.
0.0	0.7995	0.003441	0.537	—
0.2242	0.8010	0.01351	1.131	1.136
0.8035	0.8054	0.2143	2.331	2.314
1.663	0.8110	2.98	3.474	(3.474)

The values in the last column are calculated from the formula $\eta = \eta_0(1 + c \times 1.024)^{6.8}$;
 ak from curve = 6.72.

TABLE IV.

Highly Soluble Nitrocellulose in Acetone at 25°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.	$\text{Log } \eta \times 10^3$ calculated.
0.0	0.7881	0.003151	0.498	—
0.3037	0.7905	0.00776	0.890	0.890
0.4955	0.7914	0.01292	1.111	1.122
0.7345	0.7928	0.02387	1.378	1.381
1.301	0.7958	0.0853	1.931	1.917
1.514	0.7967	0.1214	2.084	2.097
2.068	0.8000	0.327	2.514	2.518
2.903	0.8036	1.066	3.028	3.056
3.226	0.8058	1.860	3.270	3.240
4.100	0.8097	4.585	3.661	3.680
4.436	0.8105	6.87	3.837	(3.837)

The figures in the last column are calculated from the formula $\eta = \eta_0(1 + c \times 0.4725)^{6.8}$;
 ak from curve = 3.22.

TABLE V.

Highly Soluble Nitrocellulose in Acetone at 15°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.	$\text{Log } \eta \times 10^3$ calculated.
0.0	0.7995	0.003441	0.537	—
0.3080	0.8020	0.00907	0.957	0.941
0.5037	0.8029	0.01447	1.161	1.171
0.745	0.8043	0.02803	1.448	1.433
2.098	0.8115	0.366	2.564	3.547
2.945	0.8151	1.278	3.107	3.122
4.160	0.8202	5.76	3.760	(3.760)

The values in the last column are calculated from the formula $\eta = \eta_0(1 + c \times 0.4755)^{6.8}$;
 ak from curve = 3.33.

TABLE VI.

Highly Soluble Nitrocellulose in Acetone at 0°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.	$\text{Log } \eta \times 10^3$ calculated.
0.0	0.8146	0.003979	0.600	—
0.3137	0.8170	0.01108	1.044	1.036
0.7585	0.8193	0.03732	1.572	1.563
2.136	0.8265	0.566	2.753	2.767
4.235	0.8392	9.64	3.984	(3.984)

The values in the last column are calculated from the formula $\eta = \eta_0(1 + c \times 0.505)^{6.8}$;
 ak from curve = 3.41.

TABLE VII.

Guncotton in Acetone Solution at 25°.

Concentration of guncotton. <i>C</i> .	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.	$\text{Log } \eta \times 10^3$ calculated.
0.0	0.7881	0.003151	0.498	—
0.2405	0.7892	0.00740	0.869	0.873
0.4609	0.7904	0.01531	1.185	1.178
0.6333	0.7914	0.02487	1.396	1.405
0.797	0.7923	0.03805	1.580	1.587
1.228	0.7937	0.1107	2.044	2.037
2.374	0.8011	0.9330	2.970	(2.970)

The numbers in the last column are calculated from the formula
 $\eta = \eta_0(1 + c \times 0.5905)^{6.5}$; ak calculated from curve = 3.73.

TABLE VIII.

Blasting Soluble Nitrocellulose in Ethyl Formate at 25°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.
0.0	0.9164	0.00389	0.590
0.358	0.9180	0.0447	1.650
0.717	0.9196	0.2747	2.439
1.439	0.9227	4.096	3.611

ak from curve = 7.97.

TABLE IX.

Blasting Soluble Nitrocellulose in Methyl Acetate at 25°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.
0.0	0.9213	0.00391	0.592
0.397	0.9739	0.0430	1.663
0.793	0.9265	0.2821	2.450
1.585	0.9316	3.83	3.583

ak from curve = 6.98.

TABLE X.

Blasting Soluble Nitrocellulose in Ethyl Acetate at 25°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.	$\text{Log } \eta \times 10^3$, calculated.
0.0	0.8948	0.00432	0.635	—
0.1317	0.8955	0.01297	1.113	1.118
0.2255	0.8960	0.02608	1.416	1.421
0.3841	0.8968	0.07868	1.896	1.900
0.7667	0.8988	0.755	2.878	2.854
1.209	0.9012	5.156	3.712	3.706
1.531	0.9029	17.00	4.230	(4.230)

The figures in the last column are calculated from the formula
 $\eta = \eta_0(1 + c \times 1.024)^{3.78}$; *ak* from curve = 8.52.

TABLE XI.

Blasting Soluble Nitrocellulose in Propyl Acetate at 25°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.	$\text{Log } \eta \times 10^3$, calculated.
0.0	0.8837	0.00555	0.744	—
0.1527	0.8843	0.02035	1.308	1.313
0.3876	0.8854	0.1098	2.041	2.057
0.5440	0.8861	0.309	2.489	2.482
0.7715	0.8870	1.064	3.027	3.026
0.9565	0.8879	2.407	3.381	3.423
1.390	0.8898	16.43	4.216	(4.216)

The figures in the last column are calculated from the formula $\eta = \eta_0(1 + c \times 1.024)^{9.06}$;
ak from curve = 8.77.

TABLE XII.

Blasting Soluble Nitrocellulose in Amyl Acetate at 25°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.	$\text{Log } \eta \times 10^3$, calculated.
0.0	0.8663	0.008075	0.907	—
0.1755	0.8672	0.03724	1.571	1.567
0.3046	0.8680	0.0974	1.988	1.991
0.4517	0.8688	0.2641	2.422	2.427
0.6097	0.8698	0.744	2.872	2.843
0.7502	0.8705	1.517	3.181	(3.181)

The figures in the last column are calculated from the formula $\eta = \eta_0(1 + c \times 1.024)^{9.19}$;
ak from curve = 9.37.

TABLE XIII.

Blasting Soluble Nitrocellulose in Ethyl Butyrate at 25°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	Log $\eta \times 10^3$.
0.0	0.8744	0.006253	0.7931
0.2071	0.8754	0.0388	1.589
0.394	0.8765	0.1644	2.216
0.753	0.8779	1.897	(3.278)

ak from curve = 9.65.

TABLE XIV.

Blasting Soluble Nitrocellulose in Acetoethyl-o-toluidide at 25°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	Log $\eta \times 10^3$.
0.0	1.0082	0.0995	1.980
0.2802	1.0095	0.443	2.646
0.5598	1.0107	1.362	3.134
1.117	1.0132	7.44	3.872

ak from curve = 6.03.

TABLE XV.

Blasting Soluble Nitrocellulose in Ethyl o-Tolyethylcarbamate at 25°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	Log $\eta \times 10^3$.
0.0	1.0225	0.09403	1.973
0.273	1.0241	0.892	2.950
0.402	1.0250	1.648	3.217
0.624	1.0263	4.406	3.644
0.827	1.0276	10.03	4.001

ak from curve = 10.45.

TABLE XVI.

Blasting Soluble Nitrocellulose in Ethyl Phthalate at 25°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	Log $\eta \times 10^3$.
0.0	1.1142	0.1006	2.003
0.226	1.1153	0.5485	2.739
0.399	1.1163	1.82	2.260
0.657	1.1178	10.30	4.013

ak from curve = 7.76.

TABLE XVII.

Blasting Soluble Nitrocellulose in Ethyl Acetate at 15°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.
0.0	0.9070	0.004825	0.683
0.1335	0.9077	0.01455	1.163
0.3894	0.9090	0.0934	1.970
0.7773	0.9110	0.899	2.954
1.554	0.9151	21.72	4.342

ak from curve = 8.92.

TABLE XVIII.

Highly Soluble Nitrocellulose in Ethyl Acetate at 25°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.
0.0	0.8948	0.004319	0.635
0.408	0.8967	0.02683	1.429
0.711	0.8977	0.0894	1.951
1.128	0.8994	0.294	2.469
1.683	0.9017	1.447	3.161

ak from curve = 4.61.

TABLE XIX.

Highly Soluble Nitrocellulose in Ethyl Acetate at 15°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.
0.0	0.9070	0.004825	0.6834
0.414	0.9086	0.0293	1.474
1.143	0.9016	0.3726	2.571
1.708	0.9139	2.28	3.358

ak from curve = 4.79.

TABLE XX.

Blasting Soluble Nitrocellulose in Mixture of Ethyl Alcohol and Ethyl Ether, equal volumes, at 25°.

Concentration of <i>N/C</i> .	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.
0.0	0.7541	0.004709	0.673
0.3284	0.7564	0.03997	1.602
0.5977	0.7583	0.1240	2.093
0.923	0.7606	0.539	2.732
1.087	0.7618	0.651	2.814
1.602	0.7655	5.16	3.713
1.884	0.7675	10.64	4.027

ak from curve = 7.41.

TABLE XXI.

Blasting Soluble Nitrocellulose in Mixture of Ethyl Alcohol (25 per cent.) and Ethyl Ether (75 per cent. by volume) at 25°.

Concentration of N/C.	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.
0.0	0.7335	0.003128	0.495
0.291	0.7357	0.02175	1.337
0.446	0.7364	0.05028	1.701
0.672	0.7384	0.1668	2.222
0.905	0.7401	0.5026	2.701
1.124	0.7418	1.024	3.010
1.648	0.7457	5.83	3.766
2.014	0.7487	18.46	4.267

ak from curve = 7.50.

TABLE XXII.

Blasting Soluble Nitrocellulose in Mixture of Methyl Alcohol and Ethyl Ether, equal volumes, at 25°.

Concentration of N/C.	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.
0.0	0.7564	0.003845	0.585
0.297	0.7584	0.01929	1.285
0.424	0.7594	0.03948	1.491
0.621	0.7605	0.0886	1.947
0.926	0.7626	0.278	2.444
1.237	0.7648	0.810	2.908
1.518	0.7667	1.761	3.246
2.006	0.7701	6.24	3.795

ak from curve = 6.03.

TABLE XXIII.

Blasting Soluble Nitrocellulose in Mixture of Benzyl Alcohol and Ethyl Ether, equal volumes.

Concentration of N/C.	Density.	Viscosity, η , in C.G.S. units.	$\text{Log } \eta \times 10^3$.
0.0	0.8979	0.009867	0.994
0.172	0.8992	0.03694	1.567
0.364	0.9000	0.1466	2.166
0.554	0.9027	0.4420	2.645
0.763	0.9045	1.124	3.050
1.061	0.9071	4.54	3.657
1.362	0.9100	13.29	4.123
1.722	0.9131	40.2	4.604

ak from curve = 8.53.

TABLE XXIV.

Blasting Soluble Nitrocellulose in Mixture of Methyl Alcohol and Anisole, equal volumes, at 25°.

Concentration of N/C.	Density.	Viscosity, η , in C.G.S. units.	Log $\eta \times 10^3$.
0.0	0.8923	0.007054	0.848
0.270	0.8935	0.0373	1.568
0.539	0.8947	0.1292	2.111
0.754	0.8957	0.3583	2.554
0.935	0.8965	0.6985	2.844
1.267	0.8980	1.975	3.296
1.724	0.9002	9.00	3.954
1.985	0.9040	17.62	4.246

ak from curve = 6.28.

Table XXV consists of a summary of the preceding tables.

Discussion of Results of Experiments.

The fairly close agreement between the numbers in the two last columns of tables II—VII, X—XII indicates that the viscosity of a nitrocellulose solution may, with a considerable degree of exactness, be expressed by a formula of the type $\eta = \eta_0(1 + ac)^k$. This expression is, of course, similar in form to the well-known formula of Slotte for the relation between the temperature and the viscosity of a liquid, $\eta = \frac{c}{(1 + at)^b}$.

This formula, $\eta = \eta_0(1 + ac)^k$, although applicable over a wide range of viscosity, must be regarded as empirical only—probably it is a simple form of a more general expression, applicable only when c is small. It cannot, at present, be derived from theoretical principles, although it may be deduced from the formula $\eta = a\eta_1 + (1 - a)\eta_2$, given by Lees (*loc. cit.*). This formula is, however, itself only empirical (Baker, T., 1912, 101, 1415).

As mentioned above, separate values cannot be calculated for a and k with any great degree of accuracy. This arises from the relation between the above formula and the expression $\left(1 + \frac{x}{n}\right)^n$, which, in the limit, when $n = \infty$, becomes equal to e^x , and is thus independent of n . In nearly all the cases considered at present, k lies between 6 and 9, and consequently, provided that the corresponding value of a is taken, k may vary considerably without causing a greater change in the calculated viscosities than is due to the experimental error. For this reason, separate values of a and k have been calculated only for those series in which a considerable number of experiments has been carried out. For

TABLE XXV.

Solvent.	Solute.	Density.	Viscosity.	<i>a.</i>	<i>k.</i>	<i>ak</i> from curve.
Acetone at 25°	Blasting soluble N/C	0.7881	0.003151	1.024	6.8	6.22
" " 15°	" N/C	0.7995	0.003441	1.024	6.8	6.72
" " 25°	Highly N/C	0.7881	0.003151	0.4725	6.8	3.22
" " 15°	" N/C	0.7995	0.003441	0.4755	6.8	3.33
" " 0°	" N/C	0.8146	0.003979	0.505	6.8	3.41
" " 25°	Guncotton	0.7881	0.003151	0.5905	6.5	3.73
Ethyl formate at 25°	Blasting soluble N/C	0.9164	0.00389	—	—	7.97
Methyl acetate at 25°	" N/C	0.9213	0.00391	—	—	6.98
Ethyl " 25°	" N/C	0.8948	0.00432	1.024	8.78	8.52
" " 15°	" N/C	0.9070	0.004825	—	—	8.92
Propyl " 25°	" N/C	0.8837	0.00555	1.024	9.06	8.77
Amyl " 25°	" N/C	0.8663	0.008075	1.024	9.19	9.37
Ethyl propionate at 25°	" N/C	0.8848	0.005076	—	—	9.00
" butyrate at 25°	" N/C	0.8744	0.006253	—	—	9.65
Acetoethyl- <i>o</i> -toluidide at 25°	" N/C	1.0082	0.00995	—	—	6.03
Ethyl <i>o</i> -tolylethylcarbamate at 25°	" N/C	1.0225	0.09403	—	—	10.45
" phthalate at 25°	" N/C	1.1142	0.1006	—	—	7.72
" acetate at 25°	" N/C	0.8948	0.00432	—	—	4.61
" " 15°	Highly N/C	0.9070	0.004825	—	—	4.79
" alcohol 50 per cent., ethyl ether	" N/C	0.7541	0.004709	—	—	7.41
50 per cent.	" N/C	0.7335	0.003128	—	—	7.50
Ethyl alcohol 25 per cent., ethyl ether	" N/C	0.7564	0.003845	—	—	6.03
75 per cent.	" N/C	0.8979	0.009867	—	—	8.53
Methyl alcohol 50 per cent., ethyl ether	" N/C	0.8923	0.007054	—	—	6.28
50 per cent.	" N/C	—	—	—	—	—
Benzyl alcohol 50 per cent., ethyl ether	" N/C	—	—	—	—	—
50 per cent.	" N/C	—	—	—	—	—
Methyl alcohol 50 per cent., anisole	" N/C	—	—	—	—	—
50 per cent.	" N/C	—	—	—	—	—

comparison between different solvents, the values of ak , obtained as described above from the different curves, have been taken.

It may be observed that the values of ak found from the curves do not always correspond with those calculated from the separate values of a and k . Since, however, the value of the differential has a definite physical meaning, whilst the separate values of a and k have been found from an empirical relation, it was considered preferable only to use the values determined from the curves for purposes of comparison.

Examination of the figures in table XXV shows that the values obtained for ak with the same sample of cellulose nitrate vary with different liquids, and further, that no obvious connexion exists between these values and other physical constants. This is well shown by comparison between acetoethyl-*o*-toluidide and ethyl *o*-tolylethylcarbamate, two compounds the physical properties of which are very similar, which nevertheless give widely differing values for the coefficient ak . From this it appears that the effect of cellulose nitrate on the viscosity of its solvents varies with the nature of the solvent, and does not depend merely on physical properties of the latter.

This variation in the values of $\frac{d \log \eta}{dc}$ with different solvents suggests that the condition of the nitrocellulose in solution is not the same in the various liquids. (It may be pointed out that if the concentrations are expressed in parts by weight, or if values of $\frac{dy}{dc}$ be taken, the values of the differentials will still vary with different solvents.) This must be regarded as showing that the mere act of solution produces some change in the cellulose nitrate apart from the mere physical change of state.

That a chemical change in the cellulose nitrate molecule takes place is highly improbable when it is considered that these nitrates are of considerable stability at the ordinary temperature, and that the solvents employed are indifferent liquids. In absence of acid and light, these solutions are also of considerable stability. The most satisfactory hypothesis which can be put forward to explain the behaviour of these solutions is that the nitrates of cellulose in solution are associated with the solvent, that is, the true solute is not simply nitrocellulose, but a complex of nitrocellulose and solvent. The influence of such a solute on the viscosity of the solvent would naturally depend on the nature of the compound associated with the nitrocellulose, that is, on the nature of the solvent. It is thus easy to see why in a homologous series, such as the acetic esters, the value of the differential increases as the

molecular weight increases. It cannot, however, be stated as a general rule that the higher the molecular weight of the solvent, the greater the value of the expression $\frac{d \log \eta}{dc}$.

From the results obtained by Schwarz (*loc. cit.*), there may be deduced another explanation of the difference between the rates of increase of viscosity in different solvents. It was found that when alcohol-camphor mixtures were used as solvents, the higher the proportion of camphor in the solvent, the less steep was the curve obtained by plotting viscosity against the concentration, and it was suggested that the decreased viscosity was due to the increased solvent power of the mixture containing the higher percentage of camphor. In this case it is a well-known fact that in the manufacture of celluloid gelatinisation is effected more easily by means of a concentrated solution of camphor than by a weak one.

Whilst in the case of a crystalloid the solubility in any ordinary solvent is a matter of easy determination, and is under definite conditions a constant, the determination of the solvent power of a liquid for substances, such as nitrocellulose, is impossible. By arbitrary tests it is possible to get a rough comparison between different solvents, according to their behaviour with different varieties of cellulose nitrates. Thus, a liquid dissolving the so-called insoluble nitrocellulose (guncotton) has a higher solvent power than one which dissolves only the lower nitrates.

Unfortunately, all the simple solvents examined above have been found to gelatinise guncotton, consequently, comparison between them in this way is impossible. Nevertheless, the above results are, on the whole, in favour of the theory of Schwarz, whilst other facts may be brought forward in its support.

For example, acetoethyl-*o*-toluidide, which gives the lowest value observed for *ak*, is one of a class of compounds which are known to be good solvents for cellulose nitrates, its phenyl analogue being used, to some extent, as a gelatiniser for celluloid under the name "mannol."

It has been pointed out that in the homologous series of the esters the value of the differential increases with the molecular weight. The higher members of this group are not solvents for nitrocellulose, and it is only reasonable to suppose that in the case of this group of substances the solvent power diminishes regularly as the molecular weight increases. Again, glyceryl trinitrate, which is a poor solvent for cellulose nitrates, yields with low proportions of this blasting soluble nitrocellulose extremely viscous solutions—firm jellies, in fact.

Mixtures of ethers and alcohols give results for the viscosity

constants much lower than is to be expected from the comparatively low solvent power of such mixtures. If, however, the view is adopted that the solvent power of these mixtures is due to the formation of an ether-alcohol complex (Baker, *loc. cit.*), then abnormal results are to be expected, owing to the fact that only a portion of the solvent is thus associated. The solvent power of such a mixture will, owing to the want of solvent power, both of alcohols and ethers, be less than that of the complex itself.

Thus, the above results for simple solvents, though not in themselves conclusive, at least are not contrary to the suggestion of Schwarz, that the fluidity of a solution of nitrocellulose in a solvent is a criterion of the gelatinising or solvent power of the liquid.

The viscosity of a cellulose nitrate solution of definite content depends, to a large extent, on the nature of the cellulose from which the nitrate is derived. Oxy- and hydro-celluloses give nitrates the solutions of which possess extremely low viscosity (Berl and Klaye, *Zeitsch. Schiess. Sprengstoffwesen*, 1907, **2**, 381).

It is generally supposed that the high viscosities of cellulose nitrate solutions are due to the high molecular weight of the cellulose nitrate, and that the lowering of viscosity observed in the case of oxy- and hydro-cellulose nitrates is due to a diminution in the size of the molecule. The molecular weight of the cellulose nitrate is naturally dependent on that of the original cellulose, and, consequently, it is to be expected that solutions of cellulose and its derivatives (oxy- and hydro-celluloses) in ammoniacal copper oxide should have viscosities not far removed from those of solutions of cellulose nitrates of the same concentration.

Ost (*Zeitsch. angew. Chem.*, 1911, **24**, 1892) has shown that, as with solutions of the nitrates, solutions of oxy- and hydro-celluloses in ammoniacal copper oxide solution have low viscosities.

The last-named author found, however, that mercerised and untreated cellulose gave practically the same viscosities in solution, and from this deduced that mercerisation was not accompanied by chemical change.

This theory is totally opposed to that of Berl (*Zeitsch. Schiess. Sprengstoffwesen*, 1909, **4**, 81), who showed that the nitrates of mercerised cellulose were much less viscous in solution than those of normal cellulose, prepared under the same conditions.

In order to investigate the cause of this discrepancy, a sample of cop waste was mercerised by treatment with a 40 per cent. solution of sodium hydroxide and nitrated, the original cellulose being nitrated under the same conditions. The resulting nitro-

celluloses were stabilised by boiling with water, and the viscosities of 1 per cent. solutions in acetone determined:

Composition of mixed acid.	Material nitrated.	Viscosity of 1 per cent. solution, acetone=1.
HNO ₃ 24.0	Normal cellulose	1315
H ₂ SO ₄ 68.0		
H ₂ O 8.0		
HNO ₃ 24.5	Mercerised cellulose	29.3
H ₂ SO ₄ 63.6		
H ₂ O 11.9		
HNO ₃ 24.6	Normal cellulose	791
H ₂ SO ₄ 60.4		
H ₂ O 15.0		
HNO ₃ 24.6	Mercerised cellulose	21.7
H ₂ SO ₄ 60.4		
H ₂ O 15.0		
HNO ₃ 24.6	Normal cellulose	405
H ₂ SO ₄ 60.4		
H ₂ O 15.0		
HNO ₃ 24.6	Mercerised cellulose	16.7
H ₂ SO ₄ 60.4		
H ₂ O 15.0		

The viscosities of cellulose and mercerised cellulose in 1 per cent. solution in ammoniacal copper oxide were found by Ost to be from 25—30, taking the viscosity of the solvent as unity, a number far below that of a 1 per cent. solution of a normal cellulose nitrate.

It is hardly conceivable that the process of nitration, or rather of esterification, should produce an increase in the size of the cellulose molecule sufficient to explain the high viscosities of the cellulose nitrate solutions as compared with the viscosities of the solutions of cellulose observed by Ost, and it is also well known that the process of stabilisation has a tendency to decrease viscosity, so that it is reasonable to suppose that normal cellulose has a molecular weight corresponding with a viscosity of at least as high an order as that observed with solutions of its nitrates. Mercerised cellulose, on the other hand, gives values for its viscosity of the same order, whether in solution as a nitrate or in ammoniacal copper oxide.

From the above considerations it would appear that the identity of the viscosities observed by Ost of normal and mercerised cellulose in solution in ammoniacal copper oxide is due, not to a chemical identity of these substances, but rather to a change in normal cellulose preceding or accompanying solution in the above reagent. This change is probably the same as that accompanying mercerisation, and therefore the suggestion of Cross and Bevan (*Ber.*, 1909, **42**, 2198) to compare the densities of solutions of cellulose and mercerised cellulose cannot be expected to yield any useful results.

Influence of Association on Viscosity.

The influence of association on viscosity has been demonstrated by a number of workers. In particular, Dunstan and Wilson (*T.*, 1907, **91**, 89) have pointed out that whilst in the case of

unimolecular liquids at a particular temperature the value $\frac{\eta}{\text{molecular volume}}$ is approximately constant, associated liquids give higher values, values which depend to some extent on the degree of association.

Differentiation between the two classes of liquid, associated and non-associated, appears to rest entirely on physical evidence such as the above.

Various relations between the molecular weight or volume and some physical property of a liquid have been observed to hold for a large number of liquids; in other cases, conformity with the rule can only be secured by assuming a larger molecular weight than that indicated by the chemical properties. To account for this, such compounds in the liquid state are generally supposed to exist, partly or entirely as aggregates of two or more molecules, and are said to be associated. No evidence, other than physical, has, however, been put forward in favour of the existence of these definite molecular aggregates.

As mentioned above, associated liquids give abnormally high values for the expression $\frac{\eta}{\text{molecular volume}}$. Whilst, of course, values higher than the normal might well be expected in the case of a liquid containing molecular aggregates, yet, unless we assume enormously high values for the molecular weight, it is impossible to bring associated liquids into conformity with this rule. For example, in the case of water, the average number of molecules in the aggregates would require to be about eight, in the case of glycerol several hundred. These numbers are far larger than those obtained by other methods, such as the surface tension or molecular co-volume method.

Thus it appears that the assumption of the existence of aggregates of molecules in associated liquids is based on physical and not chemical evidence, and further, that it is incapable of explaining the fact that associated liquids give very high viscosities.

The physical properties of liquids from which is derived all our evidence on the subject of association themselves depend ultimately on the attraction between the molecules of liquids. Our knowledge of the laws of molecular attraction is comparatively slight, but the intimate relationships which appear to exist between the molecular weight or volume and certain physical properties in the case of unassociated liquids indicate that in such liquids at least the molecular attraction is a definite function of the molecular weight, and depends merely on the mass of the molecules and the distance between them.

Associated liquids possess one characteristic in common; the molecules of all of them, without exception, contain some grouping known to possess considerable residual affinity. If now, in addition to the above-mentioned molecular attraction, it is assumed that these groupings possess for each other an attraction similar in its nature to molecular attraction, that is, a force between each centre of attraction and all other centres within its sphere of influence, but dependent on the nature of the grouping, the laws, not merely of molecular attraction but those governing the physical properties, will naturally be modified by the existence of this new form of molecular attraction.

Whilst our knowledge of the exact nature and amount of molecular attraction is too limited to apply any quantitative test to the above assumption, the direction in which the physical properties of a liquid would be modified in the case of a compound of the above-described type may be investigated.

In the first place, the increase in the amount of the attraction between the molecules due to residual affinity will naturally decrease the readiness with which such molecules part from each other, consequently the vapour tension of an associated liquid will be lower, that is, the boiling point higher than if it were not associated.

Also, if the attraction between the molecules of a liquid is increased, they will naturally tend to approach each other more closely, and, consequently, the density will increase. From this it appears that the residual affinity attraction will tend to make the density of an associated liquid higher than that calculated (compare Traube, *Ber.*, 1895, **28**, 2728), and, consequently, the molecular co-volume, $\frac{M}{d} - \sum nc$, will be less than the normal, and this is actually observed with associated liquids.

The viscosity of a fluid appears to be due to collisions between the molecules of the moving fluid, consequently any factor which tends to increase the number of such contacts will naturally increase the viscosity. Molecular attraction, by which a moving molecule is liable to be deviated towards a second molecule and thus coming into contact, is thus a prominent factor in determining the number of such contacts, and an increase of this attraction above the normal value will result in an increase in viscosity above that which is to be expected from the normal molecular volume.

According to the generally adopted method of regarding associated liquids as containing aggregations of moléculés, the degree of association is regarded as the average number of molecules in each aggregate. This number is determined generally from the

value which must be assumed as the molecular weight of the liquid under consideration in order that a relation between some physical property and the molecular weight may be satisfied by experimental results.

The hypothesis put forward above necessitates that a new interpretation shall be given to this number, and it at once appears that the degree of association is a measure of the effect of the attraction due to residual affinity.

Since different physical properties depend in totally different ways on molecular attraction, it is not difficult to realise that numerical results for this degree of association will necessarily differ with the nature of the property used as the basis of determination of such numbers.

The degree of association of a liquid diminishes with increase of temperature. This does not necessarily mean that the formula representing attraction due to residual affinity is a function of the temperature, as the increased distance between the molecules at higher temperatures naturally diminishes its actual value, whilst the increased kinetic energy of the molecules lessens the apparent effect, and both of these naturally result in a diminution in the experimentally determined degree of association.

The above hypothesis of increased molecular attraction due to residual affinity may be applied to mixtures of liquids. Thus, when two liquids, such as water and alcohol, are mixed, the residual affinities of both liquids serve as centres of mutual attraction, and the result, as shown by viscosity determinations (Dunstan, T., 1909, 95, 1556), is a high degree of association. On the other hand, if one liquid has no residual affinity, the association of the other liquid is decreased, owing to the decrease in the number of molecules within the range of attraction of each molecule possessing residual affinity. Consequently, in such a case, the viscosity-composition curve would sag considerably, or even give minimum values, such as are actually observed in certain cases.

Summary.

The viscosities of solutions of cellulose nitrates at various concentrations in a number of liquids have been determined, and are found to follow the law $\eta = \eta_0(1 + ac)^k$, where a and k are constants dependent on the nature both of solvent and solute. For comparing different solvents the value of $\frac{d \log \eta}{dc}$ was found to be the most convenient characteristic.

The value of this constant for the same nitrocellulose varied with different solvents, and the results were, in general, in agree-

ment with the view that the better the solvent the less the viscosity.

The conclusion arrived at by Ost that cellulose and mercerised cellulose are identical from a chemical point of view is untenable in view of the results obtained by a study of the viscosities of solutions of their nitrates.

A fresh hypothesis has been put forward to account for the phenomena of association.

The author is indebted to Colonel Sir Frederic L. Nathan and to Messrs. Nobel's Explosives Co. for facilities for carrying out the above investigation, and also for permission to publish these results.

ARDEER.

CLXXXI.—*Adiabatic and Isothermal Compressibilities of Some Liquids Between One and Two Atmospheres Pressure.*

By DANIEL TYRER.

THE compressibility of liquids is as yet a property which has been very little investigated. This has been due partly to the experimental difficulties and partly to the requirement of large and expensive apparatus for such work. A comparison of the results of different observers is sufficient proof of the difficulty of obtaining accurate results. The divergences shown by the results of different investigators appear to be greater at the smaller pressures than at the higher pressures. This is due to two reasons; first, when the pressure is small the volume change is correspondingly small, and hence more difficult to measure accurately, and secondly, because the latent heat evolved due to the contraction of the liquid is so small for a small change in volume that it requires a long time for it to pass away, and the exact attainment of the original temperature becomes a matter of very considerable difficulty. For instance, in an average case, 1 c.c. of a liquid subjected to a change in pressure of one atmosphere undergoes a volume change of about 0.0001 c.c., and a rise in temperature of about 0.01°. This rise in temperature would cause roughly a volume change of 0.0001 c.c., that is, about 50 per cent. of the total change. It will be easy to understand, therefore, that in measuring isothermal compressibilities at low pressures with even only a moderate degree of accuracy, it is necessary to detect and obviate exceedingly small

temperature changes. It will be also easy to understand that for small pressures at least, the measurement of the adiabatic volume change is a much simpler matter, and from the adiabatic compressibility we can calculate, by aid of a sound thermodynamic equation involving only quantities susceptible of accurate measurement, the ordinary isothermal compressibility. This method, therefore, promises to yield results for low pressures, of a much higher degree of accuracy than is attainable by direct measurement. It was the object of this work to investigate this method.

Apart, however, from the advantage of being able to determine isothermal compressibilities from the results, the adiabatic compressibility of a liquid is of considerable interest and importance in itself, and it is at present an entirely uninvestigated property.

In studying either the adiabatic or isothermal compressibility of liquids from a chemical point of view it is necessary to compare the values for different liquids at a standard condition of pressure, and the most suitable and scientific condition is when the external pressure is zero, for then a liquid is subject only to internal forces. Practically, it is impossible to determine compressibilities at this condition, but since the compressibility varies but slightly with the pressure, the results obtained for very low pressures (1 to 2 atmospheres) will satisfy all the requirements, and will differ but slightly from the results for a zero pressure.

Method and Apparatus.

The principle of the method consists simply of subjecting the liquid contained in a suitable vessel to a change in pressure of about one atmosphere, and then measuring the volume change before any of the heat produced in the compression has been lost. Practically, it was found better to measure the volume change on release of the pressure instead of on compression. The rapidity of the operation ensures a true adiabatic condition. The details of the method are best explained by reference to the diagram.

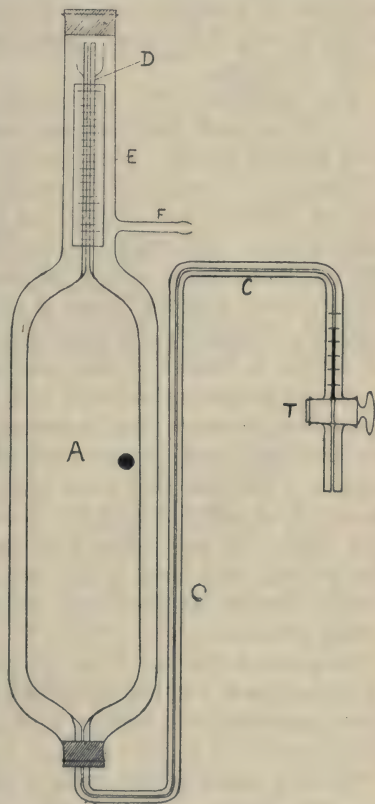
Two compressibility instruments or piezometers were used, one of glass (ordinary soft soda-glass) and the other of copper. The glass piezometer consists of an inner vessel *A* of about 500 c.c. capacity. This is enclosed in an outer vessel *B* of any convenient size. The one end of *A* is brought out to a fine capillary tube *C* provided with a tap *T*. The other end of *A* is brought out to another capillary tube *D* open at the end. This tube has been accurately calibrated, and has fixed behind it in an immovable position a glass scale graduated in half-millimetres. The vessel *A* is filled with the liquid to be investigated by aid of the tube *C* to some point in the calibrated tube *D*. The end of the tube *E* is provided with a

rubber stopper fastened down in a suitable manner to prevent it being blown out. The tube *F* is attached by means of stout rubber tubing to a manometer and a small compression air-pump. A pressure of about one atmosphere is applied, and the level of the liquid in the tube *D* is depressed a few centimetres. When the temperature is constant the height of the liquid in *D* is read, and then the pressure is suddenly released by turning a side-tap. The level of the liquid in *D* immediately rises, and its new position is quickly noted. From this the change in volume is determined, and the pressure change is found from the manometer readings. These are all the data required.

The piezometer is placed in a thermostat consisting of a 50-litre water-bath provided with stirrer and thermo-regulator.

It will be observed that the pressure is always the same on the outside and on the inside of the vessel *A*, and thus any dilatation of the glass vessel on the change of pressure is avoided. B

There is only one correction to be made to the results, and that is for the change in volume which the piezometer itself undergoes, due to the compressibility of the glass of which it is made. This is a larger correction than might at first sight appear. The cubical compressibility of glass according to Amagat (*Compt. rend.*, 1889, 108, 1199) is 0.0000022. Hence, for a pressure of one atmosphere the change in capacity of the piezometer (500 c.c. volume) is 0.00110 c.c., and this for an average case amounts to about 3 per cent. of the total volume change. Now the compressibility of glass, like the coefficient of thermal expansion, varies rather considerably with the nature and history of the glass. Hence to avoid errors on this matter, and also to test some other doubtful points, it was decided to make a copper piezometer and to repeat some of the determinations with this instrument.



The copper apparatus is similar in principle to the glass one, but differs a little in construction. It consists of an inner copper vessel of about 600 c.c. capacity supported in an outer enclosing vessel on a single pivot point, and brought out at the upper end to a slightly conical brass tube, into which was carefully ground a glass attachment carrying the calibrated capillary tube in which the volume change is measured. A wider glass tube by which connexion is made to the pump and manometer is screwed down air-tight on a rubber bed to the outer vessel of the instrument. In other details the copper piezometer is like the glass one already fully described.

The compressibility of copper (85×10^8 according to Amagat, *loc. cit.*) is much smaller than that of glass, and hence the correction for the change in volume of the piezometer under the change of pressure is considerably smaller. Also, as the copper apparatus was of different construction, of a different volume, and was fitted with a wider calibrated capillary tube, every opportunity was given for any constant errors in the method to manifest themselves. As will be seen, however, there is an excellent agreement between the results obtained by the glass and by the copper piezometers. It is, of course, a matter of the greatest importance to have the liquid in the piezometer absolutely free of entrapped air. With the glass apparatus it was a simple matter to effect this, for any entrapped air bubbles could be perceived and easily removed, but with the copper apparatus this point gave a great deal of trouble as small air bubbles adhered very firmly to the comparatively rough sides of the vessel. It was found best carefully to remove all dissolved air by boiling, and then if any small air bubbles were entrapped it would dissolve in the liquid on keeping, especially when under a small pressure.

To prevent the tap *T* of the glass apparatus from leaking under the pressure it was lubricated with a warm mixture of glycerol and dextrose, which on cooling became almost solid. This lubricant is quite insoluble in the organic liquids used in these experiments. With the water experiments a semi-solid fat had to be used. To make further certain that the tap did not leak (it is obviously of the greatest importance that it should not leak, however slightly), the capillary tube just above the tap was graduated in millimetres and filled (after the liquid to be investigated) to any point, with a thread of mercury. Any depression of the mercury under the pressure proved the tap to be leaking. However, after taking these precautions, this point gave no trouble whatever.

In the early experiments it was always noticed that when the

pressure was released the level of the liquid in the calibrated capillary tube *D* rose immediately to a certain point and then began quickly falling for two or three millimetres. The cause of this fall after the pressure was released was found to be due to a slight cooling owing to the evaporation of a film of moisture on the outside of the inner vessel. If the air contained in the space between the inner and outer vessels of the piezometer was carefully dried, the after-fall of the level of the liquid was greatly diminished, but still not entirely obviated. If the space between the two vessels was filled with water, then not the slightest trace of this "after-fall" was observable; but if the experiments were carried out with this space filled with water instead of air it became a question as to whether the results would be strictly adiabatic. To satisfy myself on this point a series of experiments was carried out on benzene with: (a) the space between the two vessels filled with dry air, the maximum rise of the liquid in the tube being taken as correct; (b) the space between the two vessels filled with water; and (c) the space between the two vessels filled with petroleum. Further, all three conditions were repeated with the copper apparatus. In the following table are given the adiabatic compressibilities of benzene obtained under the three conditions.

Temperature.	Adiabatic compressibility $\times 10^6$.					
	Glass apparatus.			Copper apparatus.		
	(a).	(b).	(c).	(a).	(b.)	(c).
9.5°	61.10	61.17	61.22	61.25	61.00	61.10
48.3	82.95	83.02	83.12	82.88	82.90	82.90

The differences between the results for the different conditions are very small and within limits of experimental error. It can be safely concluded that in each case the operation is strictly adiabatic. It was found best to have the space between the two vessels of the piezometers filled with heavy petroleum, as this did not evaporate at the higher temperatures.

A further point to be considered is whether the piezometer itself changes in temperature along with the liquid on release of the pressure. On a rough calculation for ether at 0° I find that when a pressure of 1 atmosphere is released there occurs a fall in temperature of about 0.019°. If this change communicates itself to the walls of the containing vessel it will cause a slight diminution of the capacity, and hence a too large expansion of the liquid. In the second of time required for the release of the pressure and reading of the height of the liquid, however, no appreciable cooling of the vessel itself can occur, protected as it is by the film of liquid lying

in immediate contact with its surface. This conclusion is also justified by the fact that the results obtained by the two piezometers agree well, whereas the correction in one case, if it existed, would be twice as great as in the other case. In any case, were the glass vessel to cool by the same amount as the liquid, it would only mean a correction to the result of 0.5×10^6 .

Calibration of the Capillary Tubes.

In the early experiments the change of volume occurring on release of the pressure was determined by weighing a certain quantity of mercury which was displaced in the expansion. It was found better, however, to measure directly the change of volume in a calibrated tube of convenient diameter. In order to have a conveniently large depression for a pressure of one atmosphere it was found necessary to have a rather narrow capillary tube, and this introduced the question as to whether capillary forces and liquid clinging to the sides of the tubes would not introduce considerable errors. This point was tested by making determinations, using capillary tubes of different bore. All the results agreed excellently. The capillary tubes were calibrated by weighing threads of mercury which filled up a measured length on the scale. The calibration was done (a) with the tube dry, (b) with the tube wet with water, (c) with the tube wet with benzene. Finally, they were calibrated by fusing on one end of the tube a small glass tap, the exit tube of which was drawn out to a very fine point. The wider part of the tube near the tap was filled with pure mercury, and over it in the capillary tube was placed benzene or any other liquid. A small quantity of the mercury was run out and weighed, and the fall in the level of the liquid in the capillary tube was noted. This was done for different parts of the scale. All the methods gave results which agreed together very well, and it appeared that no appreciable quantity of liquid clung to the sides of the tube.

One unit division (0.5 cm.) of the narrower capillary tube attached to the glass apparatus gave a volume of 0.0041330 c.c.

One unit division of the wider capillary tube attached to the copper piezometer gave a volume of 0.0059142 c.c.

The volumes of the piezometers were determined by weighing the quantities of water they would hold at a known temperature. The volume of the glass instrument at 10° was found to be 499.75 c.c., and that of the copper instrument 598.31 c.c. Their volumes at other temperatures were calculated by aid of the known coefficients of expansion of glass and copper.

The pressures were measured by means of a mercury column in a U-tube of sufficiently wide bore to avoid capillarity troubles. The manometer was enclosed in a glass and wooden case to insulate it from temperature changes of the air. The pressures were read to one-tenth of a millimetre, and were all reduced to zero temperature.

Results.

If α be the adiabatic compressibility of a liquid, v the observed volume change for a change of pressure of p atmospheres, and V the total volume of the liquid, then we have

$$\alpha = \frac{v + 0.00110}{Vp},$$

where the number 0.00110 represents the correction for the compressibility of the glass of the piezometer. Amagat's (*loc. cit.*) results for the compressibility of glass and copper were taken as correct.* The corresponding expression for the copper piezometer is

$$\alpha = \frac{v_1 + 0.00051}{V_1 p_1},$$

Investigations have been carried out with the following liquids from temperatures varying from 0° to the boiling point of the liquid, or as far as the heating of the bath would allow: (1) Benzene, (2) toluene, (3) ether, (4) carbon disulphide, (5) carbon tetrachloride, (6) chloroform, (7) ethyl alcohol, (8) chlorobenzene, (9) water. In each case the liquid was very carefully purified, and the purity was tested before using by determining the density and the boiling point. The variation of the boiling point as the liquid distilled in no case amounted to more than a six or seven hundredths of a degree.

In the following tables are given the experimental values obtained (in four cases by both the copper and glass piezometers). There is an excellent agreement between the results obtained by the two instruments, and they both fall on the same curve. In later tables are given values of the adiabatic compressibility read from the smoothed curves at regular intervals of temperature.

* The values that ought really to be taken are the unknown adiabatic compressibilities. As, however, solids have comparatively slight coefficients of thermal expansion, the difference between the adiabatic and isothermal compressibilities will be very small. See thermodynamic relationship between the two compressibilities, given later.

Benzene.

With glass piezometer.		With copper piezometer.	
Tempera- ture.	$\alpha \times 10^6$.	Tempera- ture.	$\alpha \times 10^6$.
9.55°	61.17	16.15°	63.99
20.38	66.47	21.91	67.73
30.52	72.00	31.33	72.81
36.38	75.26	41.30	79.23
42.43	79.08	48.27	82.88
42.76	79.35	47.75	82.34
49.54	84.43	50.29	85.38
49.67	84.13	56.01	88.68
65.22	95.54	62.97	94.60
65.40	97.03	—	—

Ether.

With glass piezometer.		With copper piezometer.	
Tempera- ture.	$\alpha \times 10^6$.	Tempera- ture.	$\alpha \times 10^6$.
0.00°	114.1	14.75°	134.4
11.13	129.1	21.25	142.3
18.54	139.2	27.52	150.4
25.30	148.60	29.50	154.6
30.69	157.1	—	—

 α = Adiabatic compressibility.*Toluene.*

With glass piezometer.		With copper piezometer.	
Tempera- ture.	$\alpha \times 10^6$.	Tempera- ture.	$\alpha \times 10^6$.
12.42°	63.93	0.00°	58.59
16.01	65.50	12.41	63.93
27.10	70.81	38.19	75.99
38.74	76.92	47.10	81.87
50.26	83.31	57.72	88.40
60.16	90.34	67.60	96.52
61.32	91.29	79.75	106.54
68.56	96.38	90.00	114.8
84.11	109.0	—	—

Carbon tetrachloride.

With glass piezometer.		With copper piezometer.	
Tempera- ture.	$\alpha \times 10^6$.	Tempera- ture.	$\alpha \times 10^6$.
0.00°	62.82	16.16°	70.42
12.43	68.78	27.10	76.58
20.77	72.60	38.74	83.10
29.09	77.56	50.26	91.14
38.29	83.02	60.10	100.84
38.69	83.37	—	—
57.72	98.06	—	—
67.63	104.86	—	—

 α = Adiabatic compressibility.*Chlorobenzene.*

With glass piezometer.	
Tem- perature.	$\alpha \times 10^6$.
0.0°	48.92
13.40	53.73
24.24	57.21
35.53	61.44
43.97	64.97
52.79	69.10
62.02	73.78
71.69	78.24
80.47	82.6

Ethyl alcohol.

With glass piezometer.	
Tem- perature.	$\alpha \times 10^6$.
0.0°	83.47
15.52	93.80
28.41	101.34
35.28	105.28
43.54	111.66
51.90	118.2
62.05	127.6
72.31	136.6

Chloroform.

With glass piezometer.	
Tem- perature.	$\alpha \times 10^6$.
0.0°	58.80
14.14	65.35
20.96	68.38
29.42	73.34
36.77	77.48
44.80	82.27
54.58	88.62

*Carbon
disulphide.*

With glass piezometer.	
Tem- perature.	$\alpha \times 10^6$.
0.0°	52.35
12.77	57.49
12.58	57.24
20.30	60.10
29.21	63.42
33.39	64.99
40.05	68.63

 α = Adiabatic compressibility.

Water.

With glass apparatus.		With glass apparatus.	
Temperature.	$\alpha \times 10^6$.	Temperature.	$\alpha \times 10^6$.
2.40°	49.71	46.95	42.92
6.45	48.64	63.51	42.55
9.93	47.76	64.75	42.57
14.12	46.81	75.33	42.42
19.37	45.67	81.50	42.60
24.42	44.80	86.75	42.56
35.75	43.82	90.22	42.63

α = Adiabatic compressibility.

In the first four cases in which measurements have been made, both with the glass and with the copper piezometers, it will be seen that there is an excellent agreement between the two sets of values.

In all cases except water the adiabatic compressibility increases regularly with temperature, and on plotting the results it is seen that this variation is almost linear. In the case of water the adiabatic compressibility decreases with the temperature to about 72°, after which it begins to rise slightly.

The Isothermal Compressibility.

It can readily be shown thermodynamically that the following equation is true:

$$\beta = \alpha + \frac{T \left(\frac{dv}{dt} \right)^2}{JvC_p},$$

where β is the isothermal compressibility, α the adiabatic compressibility, T the temperature on the absolute scale, C_p the specific heat at constant pressure, v the specific volume, J the mechanical heat equivalent, and $\frac{dv}{dt}$ the differential of the specific volume. Knowing all the quantities in the last term of this equation, we can calculate with the help of the data already obtained for the adiabatic compressibility, the ordinary or isothermal compressibility $\left(\frac{1}{v} \left(\frac{dv}{dp} \right) \right)$. The validity of this equation rests only on the laws of thermodynamics.

In the following tables are given for the nine liquids investigated the values of the isothermal compressibility (β), calculated by aid of this equation. The values of v and C_p have been taken from data of other investigators. The values of $\frac{dv}{dt}$ have been calculated from the specific volume data in most cases by several observers,

and the mean values of concordant results taken as correct. The accuracy of these data has been very thoroughly studied, and every effort has been made to obtain trustworthy values.

Isothermal Compressibilities between 1 and 2 Atmospheres.

Benzene.

Temper- ature. $\alpha \times 10^6$.	Density.*	$\frac{dv}{dt}$.	Specific heat.‡	$\beta \times 10^6$.	Results by other observers.	
0°	56.60	0.9001	0.00131	0.3970	82.30	—
10	61.30	0.8896	0.00134	0.4027	88.45	—
20	66.25	0.8790	0.00138	0.4084	95.30	91.7 at 17.9° and 8 atmospheres [Röntgen (<i>Ann. Phys. Chem.</i> , 1891, [iii], 44, 1)].
						90.1 between 1 and 4 atmos- pheres (Pagliano and Palazzo, <i>Mem. R. Accad. Lincei</i> , 1883-4, [iii], 19, 30).
30	71.70	0.8684	0.00142	0.4141	102.68	—
40	77.75	0.8576	0.00146	0.4198	110.73	105 between 1 and 4 atmos- pheres (Pagliano and Palazzo, <i>ibid.</i>).
50	84.55	0.8467	0.00151	0.4255	120.00	—
60	92.00	0.8357	0.00156	0.4312	129.97	—
70	100.35	0.8248	0.00164	0.4369	142.47	122 between 1 and 4 atmos- pheres (Pagliano and Palazzo, <i>ibid.</i>).

* Young (*Sci. Proc. Roy. Dubl. Soc.*, 1910, 12, 374).

† These values are the mean results calculated from the experimental data of Young (*ibid.*) and Kopp (*Ann. Phys. Chem.*, 1847, [ii], 72, 1, 223).

‡ Mills and McRae (*J. Physical Chem.*, 1910, 14, 797).

Chlorobenzene.

Temper- ature. $\alpha \times 10^6$.	Specific volume.*	$\frac{dv}{dt}$.†	Specific heat.‡	$\beta \times 10^6$.	Results by other observers.
0° 49.05	0.8666	0.03850	—	—	64.3 [Biron (<i>J. Russ. Phys. Chem. Soc.</i> , 1912, 44, 65)].
10 52.30	0.8952	0.03867	—	—	66 at 13° and 9 atmospheres [Suchodski (<i>Zeitsch. physikal. Chem.</i> , 1910, 74, 257)].
20 55.70	0.9040	0.03880	0.315	74.9	—
30 59.35	0.9129	0.03895	0.322	79.3	—
40 63.35	0.9220	0.03910	0.328	84.0	—
50 67.75	0.9309	0.03925	0.335	89.1	—
60 72.45	0.9402	0.03945	0.343	94.7	—
70 77.50	0.9500	0.03975	0.350	101.2	—
80 82.85	0.9598	0.001015	0.358	108.4	—

* Young (*loc. cit.*)

† Calculated from Young's experimental data.

‡ Schiff (*Zeitsch. physikal. Chem.*, 1887, 1, 376). Only three determinations were made. The results given were read from a curve drawn through these three points.

Toluene.

Temperature. $\alpha \times 10^6$.	Specific volume.*	$\frac{dv}{dt}$.†	Specific heat.‡	$\beta \times 10^6$.	Results by other observers.
0° 58·59	1·1302	0·00124	0·3834	82·02	79·6 [Biron (<i>loc. cit.</i>)]. 77 at 1—4 atmospheres [Pagliano and Palazzo (<i>loc. cit.</i>)].
10 62·86	1·1426	0·00125	0·3938	86·63	—
20 67·37	1·1551	0·00126	0·4042	91·47	88 at 1—4 atmospheres (<i>ibid.</i>).
30 72·25	1·1678	0·00127	0·4147	96·69	—
40 77·35	1·1806	0·00129	0·4251	102·45	99 at 1—4 atmospheres (<i>ibid.</i>).
50 83·22	1·1936	0·00132	0·4355	109·4	—
60 90·25	1·2071	0·00138	0·4460	118·7	112 at 1—4 atmospheres (<i>ibid.</i>).
70 98·05	1·2212	0·00145	0·4564	129·3	—

* Tyrer (T., 1910, **97**, 2620).

† Calculated from experimental data of Tyrer (*ibid.*).

‡ Schiff (*Annalen*, 1886, **234**, 300). These results agree fairly well with isolated determinations by other observers.

Chloroform.

Temperature. $\alpha \times 10^6$.	Specific volume.*	$\frac{dv}{dt}$.†	Specific heat.‡	$\beta \times 10^6$.	Results by other observers.
0° 58·80	0·6551	0·0 ₃ 810	0·2323	87·27	77·8 [Grimaldi (<i>Zeitsch. physikal. Chem.</i> , 1887, 1 , 550)].
10 63·35	0·6632	0·0 ₃ 830	0·2333	93·83	—
20 68·25	0·6717	0·0 ₃ 855	0·2343	101·17	93·7 [Grimaldi (<i>loc. cit.</i>)]. 106 at 25° (extrapolated from values of Ritzel: <i>Zeitsch. physikal. Chem.</i> , 1907, 60 , 319).
30 73·50	0·6804	0·0 ₃ 884	0·2353	109·27	—
40 79·35	0·6894	0·0 ₃ 917	0·2363	118·42	123·1 [Grimaldi (<i>loc. cit.</i>)].
50 85·65	0·6988	0·0 ₃ 952	0·2373	128·34	—
60 92·40	0·7086	0·0 ₃ 990	0·2383	139·13	155·0 [Grimaldi (<i>loc. cit.</i>)].

* T. E. Thorpe (T., 1880, **37**, 196).

† Calculated from the experimental data of Thorpe (*ibid.*), Pierre (*Ann. Chim. Phys.*, 1851, [iii], **33**, 199), and Tyrer (T., 1910, **97**, 2626).

‡ Regnault (*Mem. de l'Acad.*, 1862, **26**, 262). These results agree well with isolated values by other observers.

Ether.

Temperature. $\alpha \times 10^6$.	Density.*	$\frac{dv}{dt}$.†	Specific heat.‡	$\beta \times 10^6$.	Results by other observers.
0° 114·45	0·7362	0·00203	0·5290	152·3	153·7§ (Amagat, <i>Ann. Chim. Phys.</i> , 1893, [vi], 29 , 523).
10 127·5	0·7248	0·002115	0·5349	169·0	171§ (Amagat).
20 141·0	0·7135	0·002245	0·5527	187·1	186§ „
30 156·0	0·7019	0·002390	0·5645	208·0	203§ „
35 164·4	0·6957	0·00248	0·5704	220·3	211§ „

* Young (*loc. cit.*).

† Calculated from the experimental data of Young (*loc. cit.*), Kopp (*loc. cit.*), Pierre (*Ann. Chim. Phys.*, 1845, [iii], **15**, 525).

‡ Regnault (*loc. cit.*).

§ These values were obtained by extrapolating Amagat's experimental values to a pressure of 1 atmosphere.

Carbon Tetrachloride.

Temperature.	$\alpha \times 10^6$.	Specific volume.*	$\frac{dv}{dt}$.†	Specific heat.‡	$\beta \times 10^6$.	Results by other observers.
0°	62·82	0·6125	0·0 ₃ 730	0·2010	91·42	86·8 [Biron (<i>loc. cit.</i>)].
10	67·37	0·6198	0·0 ₃ 742	0·2013	97·60	—
20	72·45	0·6274	0·0 ₃ 756	0·2016	104·50	101 [extrapolated from results of Ritzel (<i>loc. cit.</i>)].
30	78·05	0·6350	0·0 ₃ 777	0·2019	112·35	—
40	84·15	0·6428	0·0 ₃ 805	0·2022	121·9	—
50	91·10	0·6510	0·0 ₃ 837	0·2025	132·6	—
60	98·80	0·6594	0·0 ₃ 875	0·2028	144·9	—
70	107·20	0·6683	0·0 ₃ 917	0·2031	158·6	—
80	116·3	0·6772	0·0 ₃ 96	0·2034	174·8	—

* Yo LG (*loc. cit.*).† Calculated from experimental data of Young (*loc. cit.*) and Pierre (*Ann. Chim. Phys.*, 1851, [iii], 33, 199). ‡ Mills and McRae (*J. Physical Chem.*, 1911, 15, 54).*Carbon Disulphide.*

Temperature.	$\alpha \times 10^6$.	Specific volume.*	$\frac{dv}{dt}$.†	Specific heat.‡	$\beta \times 10^6$.	Results by other observers.
0°	52·85	0·7733	0·0 ₃ 880	0·2352	80·95	78·0 [Sturm and Colladon (<i>Ann. Phys. Chem.</i> , 1828, 12, 39)].
						80 at 3·3° and 8 atmospheres [Röntgen (<i>loc. cit.</i>)].
10	56·30	0·7823	0·0 ₃ 908	0·2363	86·8	—
20	59·95	0·7915	0·0 ₃ 941	0·2385	93·2	89·5 at 18° and 8 atmospheres [Röntgen (<i>loc. cit.</i>)].
						86 [Ritzel, extrapolated (<i>loc. cit.</i>)].
30	63·80	0·8011	0·0 ₃ 983	0·2401	100·6	—
40	68·35	0·8112	0·001036	0·2417	109·8	—
50	73·90	0·8218	0·001097	0·2433	120·9	—

* Pierre (*Ann. Chim. Phys.*, 1845, [iii], 15, 325).

† Calculated from Pierre's experimental data.

‡ Regnault (*loc. cit.*).*Ethyl Alcohol.*

Temperature.	$\alpha \times 10^6$.	Specific volume.	$\frac{dv}{dt}$.†	Specific heat.‡	$\beta \times 10^6$.	Results by other observers.
0°	83·50	1·2403	0·001286	0·5487	99·56	100·5 [Amagat, extrapolated (<i>loc. cit.</i>)].
						97 [Pagliano and Palazzo, 0—4 atmospheres (<i>loc. cit.</i>)].
10	89·75	1·2533	0·001325	0·5706	106·55	99·7 at 1·9° and 8 atmospheres [Röntgen (<i>loc. cit.</i>)].
						101 at 14° and 20 atmospheres [Amagat (<i>loc. cit.</i>)].
20	95·70	1·2668	0·001370	0·5950	112·95	105·3 [Pagliano and Palazzo, 0—4 atmospheres].
						115 [Amagat, extrapolated (<i>loc. cit.</i>)].
30	102·05	1·2804	0·001420	0·6208	120·64	—
40	109·00	1·2950	0·001475	0·6478	128·6	117·8 (Pagliano and Palazzo).
						129 [Amagat, extrapolated (<i>loc. cit.</i>)].
50	116·70	1·3101	0·001550	0·6762	137·9	—
60	125·25	1·3261	0·001635	0·7059	148·2	—
70	135·5	1·3430	0·00172	0·7370	158·3	—
80	144·3	1·3609	0·00181	0·7692	171·0	—

* Young (*loc. cit.*).† Calculated from Young's data. Results agree well with values calculated from data by Kopp (*loc. cit.*).‡ Regnault (*loc. cit.*).

Water.

Temper- ature. $\alpha \times 10^6$.	Specific volume.*	$\frac{dv}{dt}$ †	Specific heat.‡	$\beta \times 10^6$.	Results by other observers.
0°	50·25	1·00013	-0·0 ₄ 68	1·0091	50·28 53·1 [Amagat, extrapolated to 1 atmosphere (<i>loc. cit.</i>)].
10	47·75	1·00027	+0·0 ₄ 88	1·0020	47·80 —
20	45·60	1·00177	+0·0 ₃ 207	0·9987	45·90 50·2 (Amagat, extrapolated).
30	44·10	1·00435	0·0 ₃ 304	0·9973	44·78 —
40	43·25	1·00782	0·0 ₃ 380	0·9971	44·34 45·6 (Amagat, extrapolated).
50	42·80	1·01207	0·0 ₃ 455	0·9977	44·40 —
60	42·63	1·01705	0·0 ₃ 526	0·9988	44·82 46·2 (Amagat, extrapolated).
70	42·45	1·02270	0·0 ₃ 592	1·0001	45·29 —
80	42·55	1·02899	0·0 ₃ 655	1·0014	46·10 —
90	42·70	1·03590	0·0 ₃ 720	1·0028	47·08 —
100	42·90	1·04343	0·0 ₃ 782	1·0043	48·18 48·3 (Amagat, extrapolated).

* Taken from Landolt-Börnstein, *Tabellen*, 1912.

† Calculated from the specific volume data.

‡ Barnes and others. See Landolt-Börnstein, *Tabellen*, 1912.

In the calculation of the isothermal compressibility from the adiabatic compressibility the chief source of error lies in the term $\frac{dv}{dt}$. The determination of this quantity requires very accurate specific volume data, and relatively small errors in these data cause considerable errors in the values of the differential. Fortunately, however, differences in the specific volume data of different observers do not matter so much as irregularities in the data of each observer, and so we are enabled to calculate agreeing values for $\frac{dv}{dt}$ from data from different sources, even although they do not agree very well amongst themselves. Also it may be noted, since in the equation the term $\frac{dv}{dt}$ is squared, any error is considerably magnified.

The only other source of error lies in the value of the specific heat, and in several cases this may be fairly considerable, especially in cases of toluene and chlorobenzene, where only approximate data could be obtained. However, it is a fortunate circumstance that the terms in the equation which introduce the chief errors are additive terms in respect to the value of β which is to be determined, and so the effect of errors is much diminished; for instance,

on the average, the term $\frac{T\left(\frac{dv}{dt}\right)^2}{JvC_p}$ is about one-third the value of β , and therefore an error in this term is reduced by 66 per cent. in the calculated value of β . In the case of water, the quantity $\frac{T\left(\frac{dv}{dt}\right)^2}{JvC_p}$ is so small that all error in the calculated value of β may be considered as coming only from the value of α .

In the last column of each table have been given the values of the compressibility obtained by other investigators by direct observation. In many cases in order to make this list of results as complete as possible the values of β have been obtained by extrapolating to a pressure of 1 atmosphere the experimental results obtained at higher pressures. As the compressibility at constant temperature does not vary greatly with the pressure, no considerable error will be introduced in this operation. As will be seen from the tables, however, a satisfactory comparison of these results with those obtained in this work is not possible, as the values obtained by other observers differ so very considerably among themselves. The results of Amagat appear to be by far the most accurate compressibility values as yet obtained by the direct method, and these in the cases of alcohol, water, and ether show quite a good agreement with those obtained in this work. The results, too, of Pagliano and Palazzo between 1 and four atmospheres at the lower temperatures show a fair agreement.

It is not practicable to fix a general probable error to the values of the isothermal compressibilities obtained in this work, for this depends on the accuracy of the specific heat and $\frac{dv}{dt}$ data, which differ considerably in the different cases; for instance, in the case of ether I do not consider the probable error in the values of the isothermal compressibility to be more than a few tenths per cent., whilst in the case of chlorobenzene, in which the specific heat data are very doubtful, the probable error may be as much as 2 per cent.

Summary.

A method is described of determining the adiabatic compressibilities of liquids at a pressure of 1 to 2 atmospheres, and tables of results at different temperatures are given for: benzene, ether, chloroform, carbon tetrachloride, chlorobenzene, carbon disulphide, toluene, alcohol, and water.

From these results, by aid of a thermodynamic formula, values of the isothermal compressibility between 1 and 2 atmospheres pressure have been calculated, and tables of results for the nine cases investigated are given.

The practical portion of this work was carried out in the "Physikalische Chemie Institut" of the University of Göttingen.

CLXXXII.—*The Relation Between Residual Affinity and Chemical Constitution. Part IV. Some Open-Chain Compounds.*

By HANS THACHER CLARKE (1851 Exhibition Scholar).

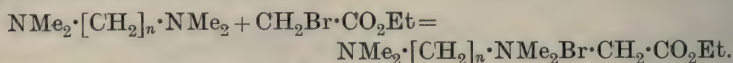
IN 1891 Bischoff, to account for certain problems of steric hindrance, put forward his "Dynamic Hypothesis" (*Ber.*, **24**, 1087), in which he embodied the idea that atoms situated in the 1:5- or 1:6-positions—or, as he termed them, *critical positions*—in carbon chains lie near to each other in space, thereby surmising that carbon chains tend to assume a cyclic form. In accordance with this theory, it would appear not unlikely that atoms endowed with residual affinity might, when situated in the critical positions, exert a more marked mutual influence than when in any other position.

This hypothesis, adumbrated by Bredig (*Zeitsch. physikal. Chem.*, 1894, **13**, 310) as a result of a study of the dissociation constants of salts of aliphatic diamines, $\text{NH}_2 \cdot [\text{CH}_2]_n \cdot \text{NH}_2$, has been brought forward by Hilditch (*T.*, 1909, **95**, 1578; *Zeitsch. physikal. Chem.*, 1911, **77**, 482) to account for the anomalous rotatory power of some optically active esters and salts of certain dicarboxylic acids; and an attempt to obtain viscometric evidence bearing on the same point has recently been described by Dunstan, Hilditch, and Thole (this vol., p. 133). This hypothesis is thus based exclusively on physical phenomena.

In an attempt to study the question from a strictly chemical point of view, the author has examined the reactive capacity of two series of compounds in which the necessary conditions are present, namely, $\text{NMe}_2 \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$, where two unsaturated atoms of the same element, and $\text{MeO} \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$, where two unsaturated atoms of different elements are separated from each other by varying numbers of methylene groups. To serve as standards of reference, by means of which it was hoped to eliminate possible differences ascribable to change in molecular weight and steric influences, the two series, $\text{CHMe}_2 \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$ (comparable with $\text{NMe}_2 \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$) and $\text{Et} \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$ (comparable with $\text{MeO} \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$), have been examined under precisely the same conditions.

The method of determining the reactive capacity was essentially the same as in the previous work (*T.*, 1910, **97**, 416; 1911, **99**, 1927; 1912, **101**, 1788); for the sake of convenience, the reactions were carried out at 0° , the solutions (1/4-molar) being standardised

at this temperature. In every case—with the diamines as well as with the monoamines—values agreeing well with the bimolecular formula were obtained; from this it must be concluded that in the ditertiary amines only one of the nitrogen atoms takes part in the reaction at the outset:



The results are therefore strictly comparable.

The refractive and dispersive power of the two crucial series of substances were also determined, but, as in the case of the cyclic compounds above quoted, no decisive regularity of anomaly was found, approximately normal values being observed in all the cases.

The numerical values obtained are set forth in the following tables:

TABLE I.

Reaction-velocity Constants, $10^3 \cdot K$.

<i>n</i> .	$\text{Et} \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$.	$\text{Pr}^\beta \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$.	$\text{NMe}_2 \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$.	$\text{MeO} \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$.
2	11.4	9.7	9.5	6.7
3	10.7	9.9	16.8	9.3
4	10.3	10.6	24.9	10.6
5	11.2	10.6	20.8	10.5
6	10.9	—	24.5	11.5
7	—	—	27.5	—

TABLE II.

Optical Constants, M and $M_\gamma - M_\alpha$.

<i>n</i> .	$\text{NMe}_2 \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$.		$\text{MeO} \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$.	
	M_α .	$M_\gamma - M_\alpha$.	M_α .	$M_\gamma - M_\alpha$.
2	37.39	1.185	30.71	0.974
3	42.12	1.279	35.86	0.766
4	46.40	1.382	39.87	1.186
5	51.07	1.407	44.63	1.215
6	55.84	1.618	49.32	1.685
7	60.03	1.720	—	—

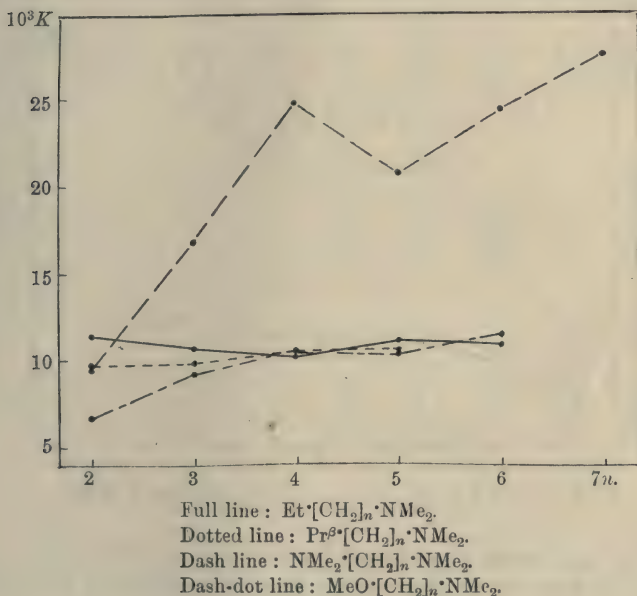
From table I it will be seen that the reactive power of the normal ($\text{Et} \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$) series remains fairly constant, barely altering with increase of length of chain; in the *iso*-series ($\text{Pr}^\beta \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$) the values increase very slightly indeed, approaching the same value as shown by the normal compounds. It may therefore be concluded that no allowances for influences due to steric considerations and alterations in molecular weight need be made in the two principal series.

A clear idea of the relative reactivities can be formed by exam-

ination of the graphic representation (Fig. 1). In the monoamines, progression along the normal homologous series from dimethyl-*n*-butylamine to dimethyl-*n*-octylamine has negligible effect on reactive capacity. This is in harmony with the recent work of Segaller (this vol., p. 1154) on alkyl iodides. The same is observed in the *iso*-compounds; the members of this series are, on the average, slightly less reactive than the corresponding normal compounds.

In the series of ditertiary diamines, $(\text{NMe}_2 \cdot [\text{CH}_2]_n \cdot \text{NMe}_2)$, the only member displaying reactivity approximating to those of the

FIG. 1.



standards of reference is the first, which contains two methylene groups. The succeeding members tend to increase in reactivity with increasing numbers of methylene groups in the chain. The same, in a less degree, is the case in the series of methoxylated tertiary amines, $\text{MeO} \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$, which are considerably less reactive than the monoamines in the first members, but become more reactive on ascending the series.

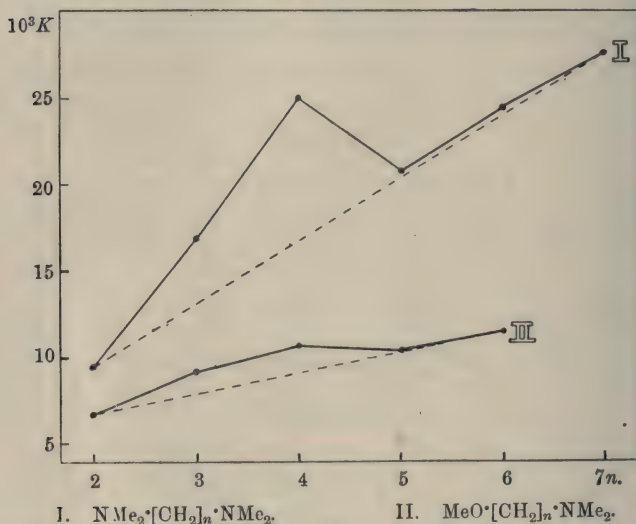
Now if it be assumed that the reactivities of members of both of these series should increase regularly with increasing length of chain, then the points representing these hypothetical reaction-velocity constants would lie near to the straight dotted lines shown

in Fig. 2, as do, in fact, those of the derivatives of pentane and hexane.

Notable exaltation of reactive capacity is exhibited by tetramethyltrimethylenediamine and tetramethyltetramethylenediamine, also by methyl γ -dimethylaminopropyl ether and methyl δ -dimethylaminobutyl ether, all of which are compounds in which the "unsaturated" atoms are relatively in the 1:5- and 1:6-positions respectively. The disposal of such atoms in the critical positions is thus seen, in both cases, to coincide with exalted reactive power.

No reason is at once apparent why the reactivities of the members

FIG. 2.



of both of these series should tend to increase with increasing length of chain, in contrast to those of the simpler normal and *iso*-tertiary amines.

EXPERIMENTAL.

Reaction-velocity Measurements.

The standard conditions, under which all the substances examined were treated in the reactivity determinations, were as follows: Equal volumes of quarter-molar absolute-alcoholic solutions of the base and of ethyl bromoacetate respectively were prepared at 0° , and mixed and maintained at that temperature. Successive portions were withdrawn at intervals, and the amount of ionisable bromine present was immediately determined by titration with $N/20$ -silver nitrate (Volhard's method). The resulting figures—with

the diamines as well as with the monoamines—were found to correspond with those of a bimolecular reaction:

$$K = \frac{1}{C_0 t} \cdot \frac{x}{a - x},$$

where C_0 represents the initial concentration of the reacting substances (1/8-molar), t the number of minutes elapsed when the determination is made, x the percentage of bromine which has been converted from non-ionisable to ionisable form, and a the initial percentage of the bromine existing in non-ionisable form (100). For the sake of convenience, the resulting velocity-constant (K) is multiplied by one thousand.

Dimethylbutylamine.

t	10	20	32	45	60	75	80	88	95	105
x	1.6	2.8	4.4	6.0	8.0	9.2	9.6	10.8	12.0	13.2
$10^3 K$...	13.0	11.5	11.5	11.4	11.6	10.8	10.6	11.0	11.5	11.6

Mean value of $10^3 K = 11.4$.

Dimethylamylamine.

t	27	39	51	61	73	84	96	107	119	131
x	3.6	4.8	6.4	7.6	8.8	10.0	11.2	12.8	13.6	14.8
$10^3 K$...	11.1	10.4	10.7	10.8	10.6	10.6	10.5	11.0	10.6	10.6

Mean value of $10^3 K = 10.7$.

Dimethylhexylamine.

t	21	32	43	54	66	76	88	100	112	124
x	2.4	4.0	5.6	6.4	8.0	8.8	10.8	11.6	12.4	13.2
$10^3 K$...	9.4	10.4	11.0	10.1	10.5	10.2	11.0	10.5	10.1	9.8

Mean value of $10^3 K = 10.3$.

Dimethylheptylamine.

t	20	34	50	65	80	95	110	125	140	155
x	2.8	4.8	6.8	8.4	9.6	11.6	13.2	14.4	16.0	17.6
$10^3 K$...	11.5	11.9	11.7	11.3	10.6	11.0	11.1	10.6	10.9	11.0

Mean value of $10^3 K = 11.2$.

Dimethyloctylamine.

t	15	30	46	60	75	90	105	120	136	150
x	2.0	4.0	6.0	7.6	9.6	10.8	12.0	14.0	15.2	17.2
$10^3 K$	10.9	11.1	11.1	11.0	11.3	10.8	10.4	10.9	10.6	11.1

Mean value of $10^3 K = 10.9$.

Dimethylisoamylamine.

t	15	30	45	60	75	90	105	120	135
x	1.8	3.6	5.2	6.8	8.4	10.0	11.2	12.4	14.0
$10^3 K$	9.8	10.0	9.8	9.7	9.8	9.9	9.6	9.4	9.7

Mean value of $10^3 K = 9.7$.

Dimethylisohexylamine.

t	22	50	71	90	110	125	143	155	170	190
x	3.2	6.0	8.4	10.4	12.4	13.6	14.8	16.0	17.2	18.8
10^3K	10.5	9.5	10.3	9.9	9.9	10.1	9.7	9.8	9.8	9.8

Mean value of $10^3K = 9.9$.*Dimethylisoheptylamine.*

t	24	45	67	90	105	120	137	151	165	190
x	3.2	6.0	8.4	10.4	12.4	13.6	14.8	16.8	17.6	19.6
10^3K	11.0	11.3	11.0	10.3	10.8	10.5	10.2	10.7	10.4	10.3

Mean value of $10^3K = 10.6$.*Dimethylisooctylamine.*

t	26	45	65	90	105	120	135	150	165	190
x	3.2	5.6	8.4	10.8	12.0	13.6	15.2	16.8	18.0	20.0
10^3K ...	10.2	10.5	11.3	10.8	10.4	10.5	10.6	10.8	10.6	10.5

Mean value of $10^3K = 10.6$.*Tetramethylethylenediamine.*

t	20	40	60	80	100	120	140	160	180	200
x	2.4	4.4	6.4	8.8	10.8	12.8	14.4	16.0	17.6	18.8
10^3K ...	9.8	9.2	9.1	9.7	9.7	9.8	9.6	9.5	9.5	9.3

Mean value of $10^3K = 9.5$.*Tetramethyltrimethylenediamine.*

t	15	30	45	60	105	120	140	160	180
x	3.0	6.0	8.4	11.6	17.6	20.0	22.8	25.2	27.6
10^3K ...	16.5	17.0	16.3	17.5	16.3	16.7	16.9	16.9	17.0

Mean value of $10^3K = 16.8$.*Tetramethyltetramethylenediamine.*

.....	20	35	45	55	65	75	85	95	105	120
x	6.0	10.0	12.0	14.8	16.8	18.8	20.8	22.8	24.4	27.2
10^3K ...	25.5	25.4	24.3	25.3	24.9	24.7	24.7	24.9	24.3	24.9

Mean value of $10^3K = 24.9$.*Tetramethylpentamethylenediamine.*

.....	15	35	50	60	70	80	90	100	110	120
x	3.8	8.4	11.2	13.2	15.6	17.2	18.8	20.8	22.4	24.0
10^3K ...	21.1	21.0	20.2	20.3	21.1	20.8	20.6	21.0	21.0	21.0

Mean value of $10^3K = 20.8$.*Tetramethylhexamethylenediamine.*

.....	15	30	40	50	60	67	75	84	95	110
x	4.4	8.4	10.8	13.2	15.6	17.2	18.8	20.4	22.8	25.2
10^3K ...	24.5	24.5	24.2	24.3	24.6	24.8	24.7	24.4	24.9	24.5

Mean value of $10^3K = 24.5$.

Tetramethylheptamethylenediamine.

<i>t</i>	16	27	36	45	60	75	89	105	122	135
<i>x</i>	5.2	8.4	11.2	13.6	17.2	20.0	23.2	26.8	29.2	32.0
10^3K ...	27.4	27.2	28.1	28.0	27.7	28.7	27.2	27.9	27.1	27.9

Mean value of 10^3K = 27.5.

Methyl β -Dimethylaminoethyl Ether.

<i>t</i>	20	40	60	80	95	110	125	140	155	170
<i>x</i>	1.6	3.2	4.8	6.4	7.6	8.4	9.2	10.4	11.6	12.8
10^3K ...	6.5	6.6	6.7	6.8	6.9	6.7	6.5	6.6	6.8	6.9

Mean value of 10^3K = 6.7.

Methyl γ -Dimethylaminopropyl Ether.

<i>t</i>	15	35	55	75	95	115	135	155	180	200
<i>x</i>	1.6	4.0	6.0	8.0	10.0	12.0	13.8	15.6	17.2	19.3
10^3K ...	8.7	9.5	9.3	9.3	9.4	9.5	9.5	9.5	9.2	9.6

Mean value of 10^3K = 9.3.

Methyl δ -Dimethylaminobutyl Ether.

<i>t</i>	24	43	58	73	86	105	120	135	150	170
<i>x</i>	3.2	5.6	7.2	8.8	10.0	12.0	13.6	15.2	16.4	18.0
10^3K ...	11.0	11.0	10.7	10.6	10.3	10.4	10.7	10.6	10.5	10.3

Mean value of 10^3K = 10.6.

Methyl ϵ -Dimethylaminoamyl Ether.

<i>t</i>	15	26	37	48	60	71	82	95	106	120
<i>x</i>	2.0	3.2	4.8	6.0	7.2	8.4	9.6	11.2	12.4	13.6
10^3K ...	11.0	10.2	10.9	10.0	10.4	10.3	10.4	10.6	10.8	10.5

Mean value of 10^3K = 10.5.

Methyl ζ -Dimethylaminoheptyl Ether.

<i>t</i>	19	41	63	80	105	136	156	177	202	229
<i>x</i>	2.8	5.6	8.4	10.0	12.8	16.4	18.0	20.4	22.8	24.4
10^3K ...	12.1	11.6	11.7	11.1	11.2	11.5	11.2	11.6	11.7	11.3

Mean value of 10^3K = 11.5.

Preparation of Compounds.

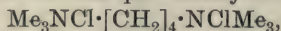
The dimethylamino-compounds above enumerated were prepared by two general methods: first, by the interaction of the corresponding halogen compound and dimethylamine; secondly, by methylation of the corresponding primary amines. This second general method may be subdivided into two separate methods: (a) methylation by heating the hydrochloride of the primary amine with formaldehyde; (b) complete methylation to the quaternary ammonium iodide by means of methyl iodide in presence of alkali,

conversion of this into the sulphide, and decomposition of the sulphide by heat.

The first of these subsidiary methods has been described by Plöchl (*Ber.*, 1888, **21**, 2117), Koeppen (*Ber.*, 1905, **38**, 882), and others for the methylation of ammonia and simple monoamines. The advantage of this method lies in the fact that the end-product consists of the hydrochloride of the pure tertiary amine, unmixed with primary, secondary, or quaternary ammonium salts. The author has found it to work fairly satisfactorily for the methylation of primary monoamines, although in every case some decomposition—resulting in the formation of trimethylamine—took place. Eschweiler, in 1893, took out a patent (D.R.-P. 80520) claiming the methylation by this method of diamines, apparently basing his claim on the formation of dimethylpiperazine from piperazine, but the present author was unable to obtain satisfactory results in attempting to apply the process to the methylation of tetra-, hexa- and hepta-methylenediamines; in every case the principal products were trimethylamine, non-volatile bases of apparently high molecular weight, and incompletely methylated substances.

In the second subsidiary method the procedure consisted in converting the quaternary trimethylammonium haloid, $R \cdot NMe_3Cl$, into the hydroxide by shaking its aqueous solution with excess of freshly-precipitated silver oxide, and thereupon saturating this solution, after filtering, with hydrogen sulphide and distilling it under atmospheric or diminished pressure. At a temperature between 200° and 230° the quaternary ammonium sulphide decomposes according to the equation $(R \cdot NMe_3)_2S = 2R \cdot NMe_2 + Me_2S$.

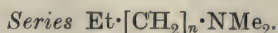
So far as the author is aware, this method, which furnishes excellent yields, has hitherto never been employed. The advantage in decomposing the sulphide in preference to the chloride is exemplified by the case of tetramethyltetramethylenediamine; Willstätter and Heubner (*Ber.*, 1907, **40**, 3869) endeavoured to prepare this base by distillation of the quaternary chloride,



but obtained only trimethylamine and methylpyrrolidine.

Decomposition of the corresponding sulphide, however, led to an excellent yield of the required ditertiary diamine.

In the following account all temperatures, unless otherwise stated, are uncorrected.



Dimethylbutylamine, $Et \cdot [CH_2]_2 \cdot NMe_2$.—From *n*-butyl iodide (1 mol.) and alcoholic dimethylamine (2 mols.), heated in a sealed

tube on the water-bath for four hours. The contents of the tube were distilled with dilute aqueous alkali, the distillate neutralised with hydrochloric acid and evaporated to dryness, the residue distilled with concentrated alkali, and the free base separated from the distillate by saturated with solid potassium hydroxide. After drying by boiling with solid potassium hydroxide and subsequently with sodium, the product boiled constantly at $95^{\circ}/761$ mm. It forms a colourless liquid of strongly basic properties and powerful odour, and is miscible with water in all proportions:

0.1242 gave 0.3232 CO_2 and 0.1692 H_2O . $\text{C}=71.0$; $\text{H}=15.1$.

$\text{C}_6\text{H}_{15}\text{N}$ requires $\text{C}=71.3$; $\text{H}=14.8$ per cent.

The *picrate* melted at 96° .

Dimethylamylamine, $\text{Et}\cdot[\text{CH}_2]_3\cdot\text{NMe}_2$.—The pure hydrochloride of *n*-amylamine (prepared by reduction of synthetic *n*-valeronitrile) was heated with an excess (about six times the weight) of formalin (40 per cent. aqueous formaldehyde) in a sealed tube for five hours at 125° . The contents of the tube were evaporated to dryness after adding a few drops of dilute hydrochloric acid, and the residue distilled with concentrated alkali. The presence of a small quantity of a gaseous base—in all probability trimethylamine—was observed. The product was worked up as described above for dimethylaminobutane. It is a colourless liquid of strongly basic properties, boiling at 122 – $123^{\circ}/755$ mm. It is soluble in water, but not miscible in all proportions:

0.1237 gave 0.3303 CO_2 and 0.1664 H_2O . $\text{C}=72.8$; $\text{H}=15.0$.

$\text{C}_7\text{H}_{17}\text{N}$ requires $\text{C}=73.0$; $\text{H}=14.8$ per cent.

The *picrate* melted at 101° .

Dimethylhexylamine, $\text{Et}\cdot[\text{CH}_2]_4\cdot\text{NMe}_2$.—The pure hydrochloride of *n*-hexylamine, prepared according to the directions of Frentzel (*Ber.*, 1883, **16**, 744) from the amide of *n*-heptoic acid, was treated as above. The product, a colourless liquid of similar properties, but less powerfully ammoniacal odour to the foregoing, boiled at 146 – $147^{\circ}/766$ mm. Another sample, prepared by methylating the hexylamine with methyl iodide and alkali, converting the quaternary ammonium iodide into the sulphide, and decomposing by heat (compare tetramethyltetramethylenediamine, below), possessed identical properties:

0.1276 gave 0.3470 CO_2 and 0.1740 H_2O . $\text{C}=74.2$; $\text{H}=15.1$.

$\text{C}_8\text{H}_{19}\text{N}$ requires $\text{C}=74.4$; $\text{H}=14.7$ per cent.

The *picrate* melted at 100° .

Dimethylheptylamine, $\text{Et}\cdot[\text{CH}_2]_5\cdot\text{NMe}_2$.—Prepared from *n*-heptyl bromide (1 mol.) and alcoholic dimethylamine (2 mols.), heated in a sealed tube on the water-bath for ten hours. It is a colourless

liquid, resembling the foregoing in general properties. It boils at $170^{\circ}/766$ mm. (corr.):

0.1297 gave 0.3579 CO_2 and 0.1721 H_2O . $\text{C}=75.3$; $\text{H}=14.8$.

$\text{C}_9\text{H}_{21}\text{N}$ requires $\text{C}=75.5$; $\text{H}=14.7$ per cent.

The *picrate* melted at 75° .

Dimethyloctylamine,* $\text{Et} \cdot [\text{CH}_2]_6 \cdot \text{NMe}_2$.—Prepared from *n*-octyl iodide (1 mol.) and alcoholic dimethylamine (2 mols.), heated in a sealed tube on the water-bath for six hours. It is a colourless liquid, possessing a faint odour, almost insoluble in water. It boils at $191^{\circ}/760$ mm.:

0.1292 gave 0.3615 CO_2 and 0.1734 H_2O . $\text{C}=76.3$; $\text{H}=14.9$.

$\text{C}_{10}\text{H}_{23}\text{N}$ requires $\text{C}=76.4$; $\text{H}=14.7$ per cent.

The *picrate* melted at 72° .

Series $\text{CHMe}_2 \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$.

Dimethylisoamylamine, $\text{Pr}^{\beta} \cdot [\text{CH}_2]_2 \cdot \text{NMe}_2$.—From *isoamyl* iodide (1 mol.) and alcoholic dimethylamine (2 mols.). It boiled at $113\text{--}114^{\circ}/770$ mm., agreeing with the observation of Collie and Schryver (T., 1890, 57, 774).

The *picrate* melted at 132° .

Dimethylisohexylamine, $\text{Pr}^{\beta} \cdot [\text{CH}_2]_3 \cdot \text{NMe}_2$.—Prepared by reduction with sodium and alcohol of *isoamyl* cyanide, and methylating the resulting *isohexylamine* by means of formaldehyde (see above). The tertiary base is a colourless liquid, which is not miscible in all proportions with water, and boils at $139\text{--}140^{\circ}/766$ mm.:

0.1319 gave 0.3583 CO_2 and 0.1777 H_2O . $\text{C}=74.1$; $\text{H}=15.0$.

$\text{C}_8\text{H}_{19}\text{N}$ requires $\text{C}=74.4$; $\text{H}=14.7$ per cent.

The *picrate* melted at 132° .

Dimethylisheptylamine, $\text{Pr}^{\beta} \cdot [\text{CH}_2]_4 \cdot \text{NMe}_2$.—*isoAmyl*acetic acid was converted into the amide by Aschan's method (Ber., 1898, 31, 2344), and this was converted into the nitrile, boiling at $178\text{--}180^{\circ}$, by distillation under diminished pressure with twice its weight of phosphoric oxide. The nitrile was reduced by means of sodium and alcohol, yielding *isheptylamine*, boiling at $146\text{--}147^{\circ}$, which was methylated by the formaldehyde method. The tertiary base was isolated as a colourless liquid, sparingly soluble in water, boiling at $162^{\circ}/765$ mm.:

0.1096 gave 0.3026 CO_2 and 0.1462 H_2O . $\text{C}=75.3$; $\text{H}=14.8$.

$\text{C}_9\text{H}_{21}\text{N}$ requires $\text{C}=75.5$, $\text{H}=14.7$ per cent.

* The dihydrodimethylconiine, boiling at $184\text{--}186^{\circ}$, described by Mugdan (Annalen, 1897, 298, 144) and shown by him to consist of a mixture of two bases, is erroneously quoted in Richter's *Lexikon der Kohlenstoff Verbindungen* (1911, 3rd Edition, II., 1528) as dimethyloctylamine.

The *picrate* melted at 86° .

Dimethylisooctylamine, $\text{Pr}^{\beta} \cdot [\text{CH}_2]_5 \cdot \text{NMe}_2$.—*iso*Hexylamine, prepared by reduction of *iso*amyl cyanide, was converted by the Schotten-Baumann method into the *benzoyl* derivative, a colourless, odourless liquid, insoluble in water, boiling at $198^{\circ}/13$ mm. This was distilled with an equimolecular quantity of phosphorus pentachloride, the distillate was treated firstly with water, to remove the phosphoryl chloride, and then with concentrated sulphuric acid, to remove the benzonitrile. After washing with dilute alkali and with water, the portion insoluble in sulphuric acid was dried and distilled. The resulting α -chloro*isohexane* (*isohexyl chloride*), which boiled in its entirety at $125\text{--}126^{\circ}/761$ mm., was shaken with a concentrated alcoholic solution of slightly more than the necessary quantity of ethyl sodiomalonate in a sealed tube in steam for four hours. From the resulting ester *isoheptanecarboxylic acid*, boiling at about 230° , was obtained in the usual manner. This was converted by Aschan's method into the amide, which was dehydrated by distillation under diminished pressure with phosphoric oxide, yielding *isoheptonitrile*, boiling at 194° . This was reduced by sodium and alcohol, yielding *isooctylamine*, boiling at $167\text{--}168^{\circ}$, which was methylated by the formaldehyde method, yielding *dimethylisooctylamine*, a colourless liquid, sparingly soluble in water, boiling at $183\text{--}184^{\circ}/767$ mm.:

0.1086 gave 0.3028 CO_2 and 0.1458 H_2O . $\text{C}=76.0$; $\text{H}=14.9$.

$\text{C}_{10}\text{H}_{23}\text{N}$ requires $\text{C}=76.4$; $\text{H}=14.7$ per cent.

In this way about 4 grams of the required tertiary base were obtained in a pure state from 20 grams of *iso*amyl cyanide; the chief losses of material occurred during the conversion of the benzoylamino-compound into the corresponding chloride, and in the interaction of this with ethyl sodiomalonate. Otherwise, good yields were obtained at all the stages.

The *picrate* melted at 69° .

Series $\text{NMe}_2 \cdot [\text{CH}_2]_n \cdot \text{NMe}_2$.

Tetramethylethylenediamine, $\text{NMe}_2 \cdot [\text{CH}_2]_2 \cdot \text{NMe}_2$.—See Clarke (T., 1912, 101, 1807).

Tetramethyltrimethylenediamine, $\text{NMe}_2 \cdot [\text{CH}_2]_3 \cdot \text{NMe}_2$.—Prepared by heating trimethylene bromide (1 mol.) with alcoholic dimethylamine (4 mols.) in a sealed tube on the water-bath for sixteen hours. The base, after drying by boiling first with solid potassium hydroxide and then with metallic sodium, boiled constantly at $144^{\circ}/760$ mm. Knorr and Roth (Ber., 1906, 39, 1428) give the

boiling point as 143—147°/755 mm. The following constants were determined:

$$D_4^{18.7^\circ} 0.7837, n_d^{18.7^\circ} 1.4215, n_y^{18.7^\circ} 1.4362.$$

The picrate melted with slight decomposition at 207° (K. and R. give 205°); the platinichloride melted and decomposed at 249° (K. and R. give 246—247°).

Tetramethyltetramethylenediamine, $\text{NMe}_2 \cdot [\text{CH}_2]_4 \cdot \text{NMe}_2$.

Tetramethylenediamine (the author desires to express his gratitude to Dr. N. Hess for the gift of a quantity of the hydrochloride of this costly base) was completely methylated by means of methyl iodide and alcoholic potassium hydroxide, according to the directions of Willstätter and Heubner (*Ber.*, 1907, **40**, 3869), and the quaternary iodide converted by means of silver chloride into the chloride, which was isolated in a pure condition. This was shaken, in dilute aqueous solution, with an excess of freshly precipitated silver oxide, the mixture filtered, and the filtrate saturated with hydrogen sulphide. This solution of the quaternary ammonium hydrosulphide was then distilled. Hydrogen sulphide was at first evolved, leaving the sulphide of the quaternary base in solution. On continuing to distil, all the water passed over without any basic co-distillate. On continuing to heat the syrupy residue, decomposition set in at about 220°, and tetramethyltetramethylenediamine and methyl sulphide passed over. It was found convenient to distil in a slow current of purified coal-gas, which was allowed to burn as it issued from the apparatus; in this way the uncondensed methyl sulphide was at once destroyed. The distillate was acidified with dilute hydrochloric acid, boiled until odourless, and the base worked up in the usual way. Its properties agreed well with those described by Willstätter and Heubner (*loc. cit.*) for the naturally-occurring substance:

	Base; b. p.	Picrate; m. p.	Platinichloride; m. p.
Natural (W. & H.)	169° (corr.)	198° (corr.)	234° (decomp.)
Synthetic	168°/762 (uncorr.)	197° (uncorr.)	238—239° (decomp.)

The following constants were determined:

$$D_4^{18.9^\circ} 0.8041, n_d^{18.9^\circ} 1.4316, n_y^{18.9^\circ} 1.4463.$$

An attempt to methylate tetramethylenediamine by heating the hydrochloride with excess of formaldehyde for five hours at 125° led to the formation of much trimethylamine, much basic oil which was not volatile with steam, and a small quantity of a liquid boiling at 162°, which on treatment with benzoyl chloride and alkali yielded an oil insoluble in water. This method was thus of no service.

Tetramethylpentamethylenediamine, $\text{NMe}_2 \cdot [\text{CH}_2]_5 \cdot \text{NMe}_2$.

α -Dichloropentane (1 mol.) and alcoholic trimethylamine (2 mols.) were heated in a sealed tube on the water-bath for nineteen hours. The contents of the tube were evaporated to dryness, leaving a hygroscopic, crystalline residue resembling the dichloride of hexamethyltetramethylenediamine. This was converted into the sulphide, and decomposed as described for the foregoing. The ditertiary base is a colourless, strongly basic liquid, miscible in all proportions with water, boiling at $190\text{--}191^\circ/766\text{ mm.}$:

0.1636 gave 0.4077 CO_2 and 0.2077 H_2O . $\text{C} = 68.0$; $\text{H} = 14.1$.

$\text{C}_9\text{H}_{22}\text{N}_2$ requires $\text{C} = 68.4$; $\text{H} = 13.9$ per cent.

$D_4^{19.3^\circ}$ 0.8033, $n_D^{19.3^\circ}$ 1.4327, $n_y^{19.3^\circ}$ 1.4475.

The *picrate* is precipitated from alcoholic solution as an oil, which rapidly becomes crystalline. It melted at 149° .

The *platinichloride* melted and decomposed at 250° .

This method of preparation was adopted because it had previously been shown (T., 1911, 99, 1432) that only small quantities of the ditertiary compound were obtained by allowing α -dichloropentane to react with piperidine, and it was to be expected that the same would occur with dimethylamine.

Tetramethylhexamethylenediamine, $\text{NMe}_2 \cdot [\text{CH}_2]_6 \cdot \text{NMe}_2$.

Hexamethylenediamine, prepared by v. Braun and Müller's method (Ber., 1905, 38, 2206), was methylated, and the quaternary ammonium sulphide prepared and decomposed exactly in the manner described for tetramethyltetramethylenediamine. A good yield was obtained of the ditertiary base, a colourless, strongly basic liquid, miscible in all proportions with water, and boiling at $209\text{--}210^\circ/765\text{ mm.}$:

0.1050 gave 0.2681 CO_2 and 0.1340 H_2O . $\text{C} = 69.6$; $\text{H} = 14.2$.

$\text{C}_{10}\text{H}_{24}\text{N}_2$ requires $\text{C} = 69.8$; $\text{H} = 14.0$ per cent.

$D_4^{14.5^\circ}$ 0.8064, $n_D^{14.5^\circ}$ 1.4366, $n_y^{14.5^\circ}$ 1.4512.

The *picrate* melted at 160° .

Tetramethylheptamethylenediamine, $\text{NMe}_2 \cdot [\text{CH}_2]_7 \cdot \text{NMe}_2$.

Heptamethylenediamine, prepared by v. Braun and Müller's method (Ber., 1905, 38, 2206) was treated exactly as the foregoing, with the only difference that the decomposition of the sulphide was carried out under diminished pressure (10—15 mm.). In this way a good yield was obtained of the required base, a colourless liquid, miscible in all proportions with water, boiling at $224\text{--}227^\circ$,

On redistillation, almost the entire quantity passed over at 228—230°/760 mm. (corr.):

0.1126 gave 0.2921 CO₂ and 0.1447 H₂O. C=70.8; H=14.3.

C₁₁H₂₆N₂ requires C=71.0; H=14.0 per cent.

D₄^{13.4°} 0.8177, $n_a^{13.4°}$ 1.4407, $n_\gamma^{13.4°}$ 1.4553.

The *picrate* melted at 120°.

Series MeO·[CH₂]_n·NMe₂.

Methyl β-Dimethylaminoethyl Ether, MeO·[CH₂]₂·NMe₂.—See Clarke (T., 1912, **101**, 1808).

Methyl γ-Dimethylaminopropyl Ether, MeO·[CH₂]₃·NMe₂.

Methyl γ-iodopropyl ether (1 mol.), prepared by Karvonen's method (*Acad. Sci. Fennicae*, A., 1912, **3**, 1; A., 1913, **104**, i, 2), was heated with alcoholic dimethylamine (2 mols.) for four hours in a sealed tube on the water-bath. The required base, worked up in the usual manner, was obtained as a colourless, strongly basic liquid, miscible in all proportions with water, boiling at 129—130°/765 mm.:

0.1063 gave 0.2397 CO₂ and 0.1251 H₂O. C=61.4; H=13.4.

C₆H₁₅ON requires C=61.5; H=12.8 per cent.

D₄^{19.7°} 0.8123, $n_a^{19.7°}$ 1.4091, $n_\gamma^{19.7°}$ 1.4224.

The *picrate* melted at 203—204°.

Methyl δ-Dimethylaminobutyl Ether, MeO·[CH₂]₄·NMe₂.

Methyl γ-iodopropyl ether (10 grams) and finely-powdered potassium cyanide (5 grams), with about 10 c.c. of dry methyl alcohol, were shaken in a sealed tube in steam for four hours. The resulting nitrile (not isolated) was reduced in alcoholic solution by means of sodium, and the resulting base (not isolated) was methylated with methyl iodide and alkali, and the quaternary ammonium sulphide prepared and decomposed in the usual manner. The tertiary base is a colourless, strongly basic liquid, miscible in all proportions with water, boiling at 150°/766 mm.:

0.1394 gave 0.3223 CO₂ and 0.1596 H₂O. C=64.0; H=12.7.

C₇H₁₇ON requires C=64.1; H=13.0 per cent.

D₄^{19.9°} 0.8228, $n_a^{19.9°}$ 1.4150, $n_\gamma^{19.9°}$ 1.4280.

The *picrate* melted at 108—109°.

Methyl ε-Dimethylaminoamyl Ether, $\text{MeO} \cdot [\text{CH}_2]_5 \cdot \text{NMe}_2$.

αε-Dibromopentane * (100 grams) was dissolved in twice to three times its volume of absolute methyl alcohol, and the mixture gently warmed on the water-bath under reflux. A solution of 10.0 grams of sodium in dry methyl alcohol, to which had been added 0.1—0.2 gram of potassium iodide, was slowly added in small portions, and the heating continued, more vigorously towards the end, until the alkaline reaction had disappeared. The bulk of the methyl alcohol was then distilled off on the water-bath, and the residue treated with just enough water to dissolve all the sodium bromide. The oil floating on the aqueous solution was separated, washed with concentrated calcium chloride solution, dried with calcium chloride, and distilled. The main portion boiled between 180° and 190° ; this was repeatedly fractionally distilled, and the fraction boiling between 183° and 187° collected. The total yield amounted to only about 40 grams of the crude product, and about 20 grams of the fraction boiling at 183 — 187° , which consisted chiefly of *methyl ε-bromoamyl ether*, probably contaminated with a small quantity of *αε*-dimethoxypentane, which, however, would not interfere with the reactions which the bromo-ether was intended to undergo:

0.1669 gave 0.1644 AgBr. Br=41.9.

$\text{C}_6\text{H}_{13}\text{OBr}$ requires Br=44.2 per cent.

Methyl *ε*-bromoamyl ether (1 mol.) was heated with alcoholic dimethylamine (2 mols.) for six hours in a sealed tube on the water-bath, and the resulting *methyl ε-dimethylaminoamyl ether* worked up in the usual manner. It is a colourless liquid, miscible in all proportions with water, boiling at 171 — $172^\circ/755$ mm.:

0.1038 gave 0.2514 CO_2 and 0.1254 H_2O . C=66.1; H=13.4.

$\text{C}_8\text{H}_{19}\text{ON}$ requires C=66.2; H=13.1 per cent.

$D_4^{19.0^\circ}$ 0.8221, $n_D^{19.0^\circ}$ 1.4199, $n_y^{19.0^\circ}$ 1.4330.

The *picrate* melted at 89° .

Methyl ζ-Dimethylaminoheptyl Ether, $\text{MeO} \cdot [\text{CH}_2]_6 \cdot \text{NMe}_2$.

A mixture of methyl *ε*-bromoamyl ether (20 grams) and finely powdered potassium cyanide (20 grams) in about 30 c.c. of pure methyl alcohol, was shaken in a sealed tube in steam for four hours. The potassium bromide and some unchanged potassium cyanide were removed, and the bulk of the methyl alcohol distilled off on

* The dibromopentane can readily be freed from benzonitrile (compare v. Braun and Steindorff, *Ber.*, 1905, **38**, 2339) by mixing with twice its volume of light petroleum and shaking this mixture repeatedly with concentrated sulphuric acid (compare Clarke, *T.*, 1912, **101**, 1805).

the water-bath. The residue was then treated with water, the oil extracted with ether, and the ethereal solution dried. On fractionally distilling, *ε-methoxyhexonitrile* was obtained as a colourless oil, boiling at 213—215°. This was reduced by means of sodium and alcohol, yielding *methyl ζ-aminohexyl ether*, a colourless, strongly basic liquid, of faint odour, miscible in all proportions with water, boiling at 186°. This base was methylated by means of methyl iodide and potassium hydroxide in methyl-alcoholic solution. On completion of the reaction the alcohol was removed in a current of steam, and the residual aqueous solution saturated with solid potassium hydroxide, whereby the quaternary iodide was salted out, and formed an oily layer floating on the strongly alkaline solution. This was separated, freed from small quantities of potassium salts by dissolving in chloroform and filtering, and finally converted into the sulphide and decomposed in the ordinary way. *Methyl ζ-dimethylaminohexyl ether* was thus obtained as a colourless, strongly basic liquid, of faint odour, boiling at 192—193°/765 mm. It is moderately soluble in water, although not in all proportions:

0.1339 gave 0.3334 CO₂ and 0.1627 H₂O. C = 67.9; H = 13.5.

C₉H₂₁ON requires C = 68.0; H = 13.2 per cent.

D₄^{10.9°} 0.8300, n_D^{10.9°} 1.4284, n_D^{10.90°} 1.4419.

The *picrate* melted at 68°.

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CLXXXIII.—*The Volatile Constituents of Coal.* *Part III.*

By ARTHUR HERBERT CLARK and RICHARD VERNON WHEELER.

FROM a study of the products of destructive distillation of coal at different temperatures and under varying conditions, the conclusion was reached (T., 1910, **97**, 1924; 1911, **99**, 649) that coal contains two types of compounds of different degrees of ease of decomposition. These two types were designated the "paraffin-yielding" and the "hydrogen-yielding" constituents respectively, thereby indicating the main gaseous products of their thermal decomposition.

V. B. Lewes ("The Carbonisation of Coal," London, 1912), whilst agreeing with our main conclusion*—that coal is a con-

* Lewes says (*loc. cit.*, p. 24): "As long ago as 1890, in a paper on 'The spontaneous ignition of coal,' read before the Institution of Naval Architects, I defined coal as being formed 'from the woody fibre and resinous constituents of a monster vegetation which flourished long before earth was inhabited by man.'"

glomerate of the degradation products of the celluloses with the partly changed resins and gums of the coal plants—disagrees with the theory that coal contains two types of compounds of different ease of decomposition. In particular, he doubts the correctness of the view that the type derived from the celluloses (named by Lewes "humus bodies") only decomposes freely above a critical temperature defined as being between 750° and 800° .

The experimental data on which this conclusion was founded have recently been confirmed in every particular by Vignon (*Compt. rend.*, 1912, **155**, 1514), who, on repeating our experiments with different coals, found the same marked increase in the quantity of hydrogen evolved between 750° and 800° as led us to surmise a "hydrogen-yielding" constituent.

We do not, however, wish to create the impression that these "hydrogen-yielding" constituents are decomposable *only* above the critical temperature (compare Lewes, *loc. cit.*, p. 215); such is not our contention, nor do we think that the statements contained in our previous papers should be construed as having such a meaning.

Our view is that these "hydrogen-yielding" constituents decompose freely at a temperature lying between 700° and 800° , yielding mainly hydrogen and the oxides of carbon. At the same time, we say (*loc. cit.*, p. 651): "It is evident that at low temperatures of distillation the paraffin hydrocarbons, and not hydrogen, are the chief products; and it seems reasonable to suppose (assuming the same compound to be responsible), that the difference is due principally to the temperature at which decomposition is effected."

Similarly, when terming the two types of compounds "hydrogen-yielding" and "paraffin-yielding," we wish to make it clear that neither hydrogen in the one case nor the paraffins in the other are found to be the *sole* gaseous products of decomposition; in the one case the product of decomposition is mainly hydrogen, in the other case it is mainly the paraffins.

In the present paper it is our intention to discuss data obtained by the destructive distillation at different temperatures of the several portions into which coal can be separated by the solvent action of pyridine and chloroform. The results, in our view, show clearly the existence of what we have termed "hydrogen-yielding" and "paraffin-yielding" substances as separate constituents of "coal"; and confirm us in the belief that the former are the degradation products of the celluloses, and the latter the resinous substances originally present in the coal plants.

This subject was touched upon in Part II of this research (p. 654), where it was recorded that the destructive distillation at 900° of that portion of coal insoluble in pyridine (a porous, coke-

like mass) yielded as gases mainly hydrogen and the oxides of carbon; whilst the portion soluble in pyridine yielded a mixture of the paraffin hydrocarbons and hydrogen.

Whilst regarding the insoluble portion of coal as most probably consisting of the degradation products of the celluloses, we hesitated to identify the soluble portion with the resinous constituents. Our hesitation was due to the fact that, like the coal from which it was obtained, the pyridine extract yielded greatly increasing quantities of hydrogen as the temperature of distillation was raised.

On continuing this work, we soon found that pyridine makes only a partial separation of the two constituents of coal—"humus" and "resinous" substances—the extract containing practically all the resinous matter, but, in addition, a considerable proportion of substances similar to the insoluble humus substances.

On treating this extract, after removal of pyridine, with chloroform or benzene, a further separation is effected, there being then obtained (1) a portion (about one-third) soluble in either chloroform or benzene, containing 80 per cent. of volatile matter, and (2) a residue, insoluble in either chloroform or benzene but soluble in pyridine, which behaves, on destructive distillation, in a manner very similar to that of the portion of the original coal that was insoluble in pyridine.

For example, on treating 100 grams of a bituminous coal with pyridine in a Soxhlet fat-extraction apparatus for several weeks, there were obtained 20 grams of extractive matter. The original coal contained 34·7 per cent. of volatile matter, as determined in the usual manner; the portion soluble in pyridine contained 53·3 per cent., and the residue insoluble in pyridine 32·2 per cent.

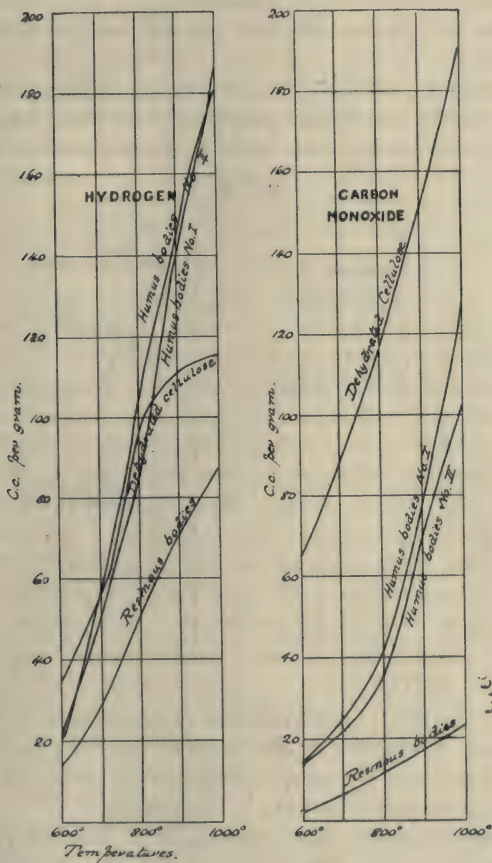
On treating 10 grams of the pyridine extract, freed from pyridine, with chloroform in a Soxhlet apparatus, 4 grams dissolved; this soluble portion contained 85·6 per cent. of volatile matter, the insoluble portion containing 31·4 per cent.

The action of chloroform on the pyridine extract is very slow, extraction of 10 grams taking about 14 days. The solution is deep orange-red in colour, and strongly fluorescent. On evaporating the chloroform, a sepia-coloured solid is obtained (light brown when powdered), which softens at 90°, and portions of which melt at 102°.

We consider that this method of treating coal—extraction with pyridine followed by extraction of the pyridine extract with chloroform—makes a complete, or nearly complete, separation between the resinous constituents and the degradation products

of the celluloses of which coal is conglomerated.* Extraction by pyridine alone does not make a complete separation, some portion of the cellulose derivatives, or humus substances, passing into solution simultaneously with the resinous substances. For there does not appear to be much difference in character, as judged by

FIG. 1.



their behaviour on destructive distillation, between the humus substances insoluble in pyridine and the substances soluble in pyridine but insoluble in chloroform (see experimental portion of this paper).

* This view receives support from the action of coal and of the several portions of coal obtained by the use of the solvents pyridine and chloroform on a sensitised plate. See Addendum to this paper.

We give in the experimental portion of this paper the results of destructive distillation at different temperatures of the separate portions of coal A, as follows:

(1) Portion of the original coal insoluble in pyridine (humus substances No. 1).

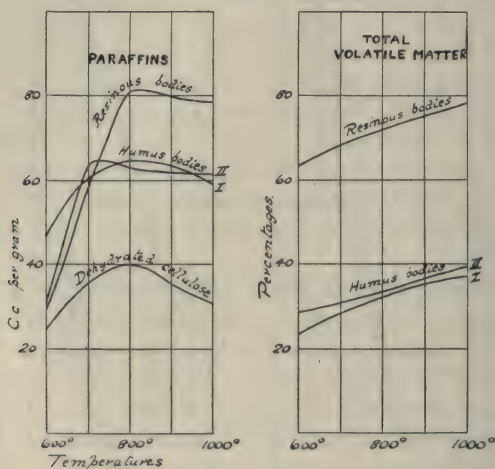
(2) Portion of the original coal soluble in pyridine (humus substances No. 2 + resinous substances).

(3) Portion of (2) insoluble in chloroform (humus substances, No. 2).

(4) Portion of (2) soluble in chloroform (resinous substances).

The main results are shown graphically in Figs. 1 and 2, which, on the one hand, bring out clearly the difference between the

FIG. 2.



portion of the original coal insoluble in pyridine and that portion soluble in both pyridine and chloroform; and, on the other hand, show the resemblance between the former of these and the portion of the pyridine extract insoluble in chloroform.

We give also for comparison the results of destructive distillation at different temperatures of dehydrated cellulose ("pseudo-carbon") prepared from filter-paper in the manner described by Cross and Bevan (*Phil. Mag.*, 1882, [v], 13, 325).

We have extended this research to the study of the liquid products of destructive distillation of coal, and hope shortly to be able to communicate the results to the Society. The examination of the chloroform extract in particular promises to yield valuable information, the "tarry matter" obtained being between 40 and 70 per cent. of the total weight distilled.

EXPERIMENTAL.

Method of Extracting the Coal.—A supply of the materials for distillation was obtained by treating the coal in the form of fine dust (passed through a sieve with 94 meshes to the linear centimetre) in separate portions of 10 grams in a Soxhlet fat-extraction apparatus, using filter-paper "thimbles." The flask of each extraction apparatus contained about 200 c.c. of pure pyridine, which was kept gently boiling on an electrically heated sand-bath, overheating being carefully guarded against. Each 10-gram portion was treated for a week continuously, the pasty mass in the thimble well stirred, and then further extracted for a week with fresh pyridine.

When extraction was complete, the solution in the flask was filtered and the pyridine distilled at a temperature of 60° , a partial vacuum being maintained in the distillation flask, and a fine stream of air being allowed to bubble through the liquid to ensure rapid evaporation. When most of the pyridine had been removed in this way, the mass remaining in the distillation flask was washed out on to a clock-glass by a fine jet of warm pyridine. Removal, so far as possible, of the last traces of pyridine was effected by heating the clock-glass at a temperature of 80° in a current of dry air, and, after grinding to a fine powder the chocolate-coloured solid thus obtained, leaving it for several weeks in a vacuous desiccator over concentrated sulphuric acid.

The residue of the coal, insoluble in pyridine, was washed with ether, and then treated in a similar manner to the dried extract.

To obtain the chloroform extract, 10 grams of the dried pyridine extract were treated in an extraction thimble in a Soxhlet apparatus with 200 c.c. of pure chloroform for two weeks on a water-bath, and the chloroform then distilled off in a partial vacuum. The chloroform extract and the residue were freed from chloroform in a manner similar to that employed for freeing the pyridine extract and residue from pyridine.

Destructive Distillation.—The coal used for the distillation experiments recorded in this paper was Coal A, from the same seam as that used in our previous work; it had the following proximate and ultimate analysis:

Proximate analysis:

Volatile matter	36.73	per cent. on ash-free dry coal.
Fixed carbon	63.27	" " "

Ultimate analysis:

Carbon	82.92	" " "
Hydrogen	5.58	" " "
Oxygen	8.45	" " "
Nitrogen	1.35	" " "
Sulphur	1.70	" " "

The apparatus employed for the distillations consisted of the platinum "retort" and tar scrubber, electric resistance furnace, and glass gas-holder, as described in a previous paper (T., 1910, 97, 1921).

(1) *The Portion of the Original Coal insoluble in Pyridine.*

Proximate analysis:

Volatile matter	34.96	per cent. on ash-free dry substance,
Fixed carbon	65.04	" " "

Ultimate analysis:

Carbon	80.81	"	"	"
Hydrogen ..	5.23	"	"	"
Oxygen	10.40	"	"	"
Nitrogen.....	2.14	"	"	"
Sulphur	1.42	"	"	"

Distillation temperature.

	600°.	700°.	800°.	900°.	1000°.
Total volatile matter { Per cent. on ash- }	24.0	29.0	32.3	35.2	37.7
Tarry matter { free dry substance }	7.0	9.3	8.1	5.5	3.8
Gas evolved per gram of ash-free dry substance, c.c. at N.T.P.	93.3	159.1	168.0	324.5	417.1

Gas analysis—

Carbon dioxide	9.80	9.00	9.55	7.00	5.35
* Ethylene	1.45	0.85	1.10	1.05	0.80
Carbon monoxide	14.30	15.15	18.25	23.10	30.80
Hydrogen	22.25	30.85	37.40	43.60	44.90
Methane.....	44.70	33.65	25.00	16.20	11.65
† Ethane	5.50	5.00	4.60	3.40	2.55
Nitrogen	2.00	4.50	4.10	6.65	4.15

* Including higher homologues and benzene.

† Including higher homologues calculated as ethane.

The coke remaining after distillation differed very little in appearance from the original substance. Practically no coking had taken place, the coke readily falling to powder.

(2) *The Portion of the Original Coal soluble in Pyridine.*

Proximate analysis:

Volatile matter	55.24	per cent. on ash-free dry substance.
Fixed carbon	44.76	" " "

Ultimate analysis:

Carbon.....	82.89	"	"	"
Hydrogen	7.14	"	"	"
Oxygen	6.62	"	"	"
Nitrogen.....	1.91	"	"	"
Sulphur	1.44	"	"	"

		Distillation temperature.				
		600°.	700°.	800°.	900°.	1000°.
Total volatile matter	{ Per cent. on ash- }	44·0	49·0	51·5	53·5	54·6
Tarry matter	{ free dry substance }	20·0	25·5	24·0	20·0	14·0
Gas evolved per gram of ash-free dry substance, c.c. at N.T.P.		62·4	127·7	175·5	246·8	302·4
Gas analysis—						
Carbon dioxide		6·90	8·00	5·70	6·50	7·05
*Ethylene		1·25	1·15	1·00	1·60	1·40
Carbon monoxide		6·90	8·40	13·85	13·80	17·40
Hydrogen		24·45	32·05	37·70	45·10	47·30
Methane		45·65	39·35	35·90	27·30	22·05
†Ethane		12·25	6·05	6·25	4·00	2·95
Nitrogen		2·60	4·80	1·20	1·70	1·85

The coke remaining after distillation was very light and much swollen, and somewhat friable.

(3) *The Portion of the Pyridine Extract insoluble in Chloroform.*

Proximate analysis :

Volatile matter	31·88 per cent. on ash-free dry substance.
Fixed carbon	68·12 " " "

Ultimate analysis :

Carbon	77·32	"	"	"
Hydrogen	5·14	"	"	"
Oxygen	14·26	"	"	"
Nitrogen	2·07	"	"	"
Sulphur	1·21	"	"	"

		Distillation temperature.				
		600°.	700°.	800°.	900°.	1000°.
Total volatile matter	{ Per cent. on ash- }	29·0	31·2	33·4	37·5	38·6
Tarry matter	{ free dry substance }	12·0	14·5	11·5	10·0	9·0
Gas evolved per gram of ash-free dry substance, c.c. at N.T.P.		99·8	162·9	225·4	305·4	381·8

Gas analysis—

Carbon dioxide	6·20	7·15	7·05	5·25	5·15
*Ethylene	1·00	1·30	0·90	0·90	1·00
Carbon monoxide	13·70	13·45	15·45	23·25	26·80
Hydrogen	26·10	35·25	45·40	47·25	47·45
Methane	43·10	33·70	23·50	17·65	14·05
†Ethane	6·80	5·80	4·15	2·65	2·05
Nitrogen	3·10	3·35	3·55	3·05	3·50

The coke remaining had a dull appearance and had not swollen; it was similar to the coke obtained from that portion of the original coal insoluble in pyridine.

(4) *The Portion of the Pyridine Extract soluble in Chloroform.**Proximate analysis:*

Volatile matter	77.33 per cent. on ash-free dry substance.
Fixed carbon	22.67 " " "

Ultimate analysis:

Carbon	85.33 " " "
Hydrogen	7.08 " " "
Oxygen	4.56 " " "
Nitrogen	1.71 " " "
Sulphur	1.32 " " "

Distillation temperature

		600°.	700°.	800°.	900°.	1000°.
Total volatile matter { Per cent. on ash- }		64.0	68.3	72.0	75.6	78.2
Tarry matter { free dry substance }		56.0	64.5	57.0	50.5	42.9
Gas evolved per gram of ash-free dry substance, c.c. at N.T.P.		55.0	104.1	164.6	189.0	221.6

Gas analysis—

Carbon dioxide	1.85	2.45	3.20	3.70	4.65
* Ethylene	6.70	7.30	5.50	5.15	8.60
Carbon monoxide	4.70	6.10	7.70	9.40	10.60
Hydrogen	26.60	25.85	32.30	37.15	39.50
Methane	35.50	43.85	40.25	35.40	31.90
† Ethane	18.60	11.30	8.50	6.50	3.50
Nitrogen	6.05	3.15	2.55	2.70	1.25

* Including higher homologues and benzene.

† Including higher homologues calculated as ethane.

The remarkable quantity of "tarry matter" obtained at all temperatures of distillation should be noted. Preliminary investigation has shown this tarry matter to consist largely of the higher members of the paraffin series of hydrocarbons.

From these tables can be calculated the volumes of each constituent gas, per gram of substance, evolved at each temperature. For the chief constituents the volumes are as follow:

	Distillation temperature.				
	600°.	700°.	800°.	900°.	1000°.
Portion No. 1:					
Carbon monoxide	13.4	25.7	40.5	74.9	128.3
Hydrogen	20.7	49.1	82.9	138.2	187.2
Paraffin hydrocarbons ...	46.8	61.5	65.6	63.5	58.5
Portion No. 2:					
Carbon monoxide	4.3	10.7	24.3	33.9	52.6
Hydrogen	15.2	40.9	66.2	111.3	143.1
Paraffin hydrocarbons ...	36.1	58.2	74.4	77.2	75.6
Portion No. 3:					
Carbon monoxide	13.4	21.9	34.8	71.0	102.2
Hydrogen	35.2	57.4	102.3	144.3	181.1
Paraffin hydrocarbons ...	30.2	64.3	62.3	61.9	61.5
Portion No. 4:					
Carbon monoxide	2.6	6.3	12.7	17.7	23.5
Hydrogen	14.6	26.9	53.2	70.2	87.5
Paraffin hydrocarbons ...	29.7	57.4	81.2	72.2	78.5

From these numbers are plotted the curves in Figs. 1 and 2; curves are also given for similar experiments with dehydrated cellulose, the details of which were as follow:

Dehydrated Cellulose.

Analysis:

Carbon	61.30	per cent. on ash-free dry substance.
Hydrogen	8.66	„ „ „
Oxygen	35.04	„ „ „

Distillation temperature.

		600°.	700°.	800°.	900°.	1000°.
Total volatile matter { Per cent. on ash- }		46.0	48.1	51.0	53.2	55.0
Tarry matter { free dry substance }		2.0	3.2	4.0	3.5	2.0
Gas evolved per gram of ash-free dry substance, c.c. at N.T.P.		216.2	298.9	379.5	419.3	462.0

Gas analysis—

Carbon dioxide	45.95	36.05	30.95	27.90	24.80
Ethylene.....	0.39	0.40	0.50	nil	0.40
Carbon monoxide	30.20	29.75	30.10	35.90	41.30
Hydrogen	9.60	19.30	26.00	26.80	24.70
Methane..	10.35	11.95	10.25	8.20	6.10
Ethane	1.25	0.65	0.35	0.15	0.60
Nitrogen.....	2.35	1.90	1.85	1.05	2.10

Addendum.

[With CLAUDE BERNARD PLATT].

The view regarding the composition of coal set forth in the preceding pages receives support from a study of the action of coal, and of the portions into which it can be separated by solvents, on a sensitised plate.

W. J. Russell (*Proc. Roy. Soc.*, 1908, B, **80**, 376) showed that simple contact between common resin and a photographic plate at the ordinary temperature for three or four days causes an action which, when the plate is developed, produces a dark picture.

The action is apparently due to some gas or vapour, for Russell found that the interposition of thin sheets of glass, mica, or aluminium prevented any action taking place. If, however, a screen of any such substance was placed between the plate and the resin, the shadow produced was not bounded by the edges of the screen, but the image was blurred as though some vapour had crept round the screen. Moreover, when a current of air was passed through powdered resin in a glass tube, action took place where the jet of air impinged on the photographic plate.

Russell also found that all ordinary coals have the property of acting on a sensitised plate in the dark when maintained at a temperature of about 50°, the pictures produced exhibiting the structure of the coal in a remarkable manner.

To prepare such photographs a surface of a lump of coal is smoothed by rubbing first on coarse and then on fine emery or glass paper. There is no necessity to polish the surface free from scratches, but it should be level. This surface is laid upon the film of a sensitised plate in a light-tight box, and kept at a temperature of between 40° and 50° for about sixteen hours. On developing the plate a picture is obtained showing streaks and patches of different intensity; parts of the coal having affected the sensitised film to a greater extent than others, and parts having no action at all.

In Fig. 1 is reproduced part of a print from a plate acted on by a lump (about 15 cm. cube) of Silkstone coal ("Coal A" of the distillation experiments). The parts of the plate acted on by the coal, which appear black on development, are white in the print.

Similarly, Figs. 2 and 3 represent the action on a sensitised plate of two small lumps of coal, a Staffordshire and a Forest of Dean coal respectively. The diffused patches of white in Fig. 2 are caused by brownish-yellow stains on the film, which close examination showed to correspond with small inclusions of pyrites in the coal.

In the light of Russell's experiments it appeared to us most probable that the markings on the sensitised plates, apart from those due to pyrites, which are readily distinguishable by their yellow colour, are caused by the resinous constituents of the coal conglomerate. If this be so, and if we are correct in assuming that the resinous constituents can be separated from the "humus substances" by treatment with pyridine and chloroform, the several portions of "coal" obtainable by means of these solvents should affect a photographic plate differently according to their nature.

To test this, we placed on the same photographic plate small quantities of the four portions of Coal A, namely:

- (a) The portion of the original coal insoluble in pyridine.
- (b) The pyridine extract.
- (c) The portion of the pyridine extract soluble in chloroform.
- (d) The portion of the pyridine extract insoluble in chloroform.

Each powder was thinly spread, (a) and (d) over an area about that of a sixpence, and (b) and (c) over about half that area, and the plate put in a light-tight box at 40° for twelve hours.

The result is shown in Fig. 4. The image of (a) is but faintly visible, whilst that of (b) is strongly brought out. Both these images are of the same size and shape as the deposits of powder that produced them.

The "chloroform extract" (c), which the distillation experiments lead us to regard as the resinous constituents of the coal, forms a

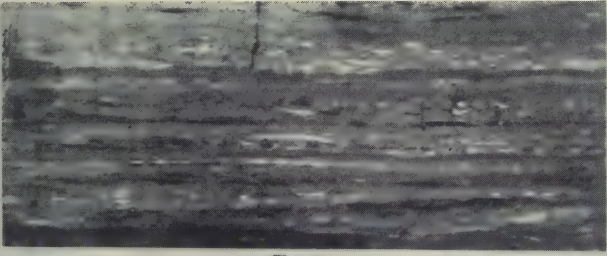


FIG. 1.

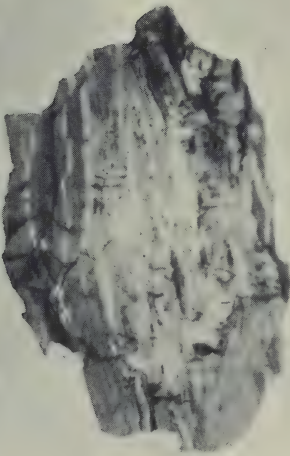


FIG. 2.

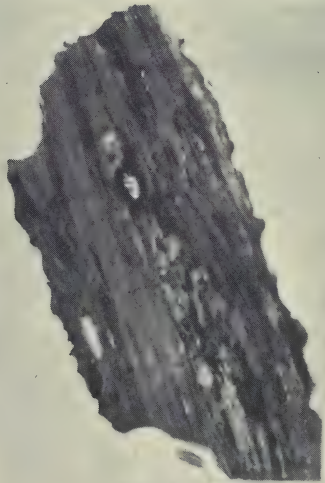


FIG. 3.



a.



b.



c.



d.

FIG. 4.

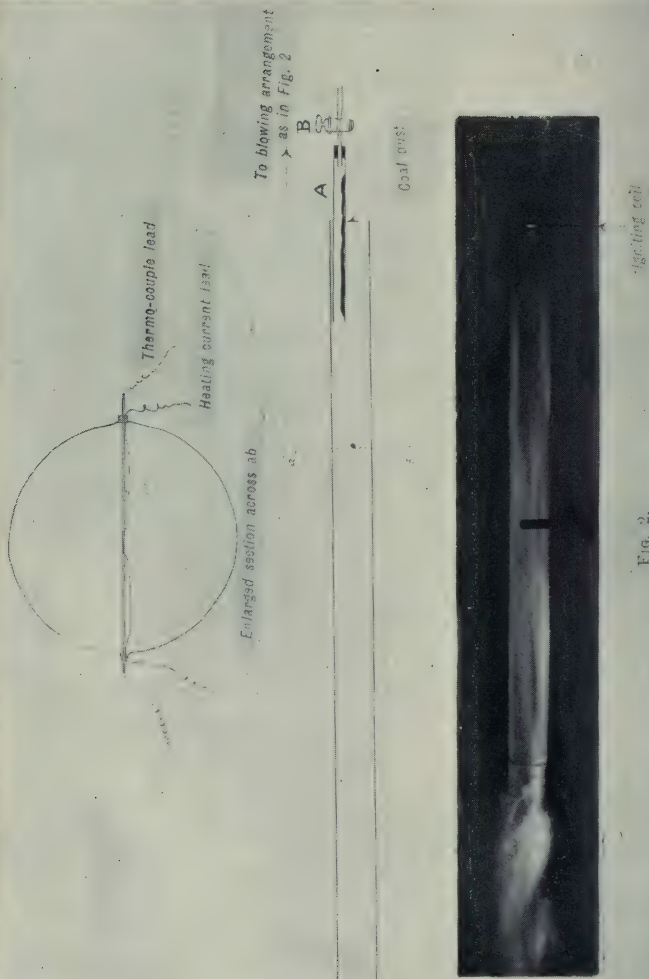


Fig. 2.

strongly marked image surrounded by an extensive "halo." The portion of the pyridine extract insoluble in chloroform (*d*), which the distillation experiments had shown to be similar in character to that portion of the original coal insoluble in pyridine, showed no image at all.

The thanks of the authors are due to the Explosions in Mines Committee of the Home Office for permission to publish these results.

ESKMEALS.

CLXXXIV.—*The Volatile Constituents of Coal. Part IV.* *The Relative Inflammabilities of Coal Dusts.*

By RICHARD VERNON WHEELER.

IF coal be regarded as a conglomerate of two main types of compounds, the one readily yielding inflammable gases and vapours on heating to a comparatively low temperature, the other requiring a higher temperature of more prolonged duration to decompose it freely, it can be understood that variations in the proportions in which these different types exist in different coals should cause corresponding variations in the chemical and physical properties of the coals.

A property, common to all coals, which would appear to depend essentially on the proportion of readily-decomposed constituents present, is their "inflammability" when in the form of dust. The author has made a number of determinations of the relative inflammabilities of dusts from different coals of known composition, which form the basis of the Second Report of the Explosions in Mines Committee of the Home Office. In the present paper the results recorded in that Second Report are discussed from a different point of view.

At the conclusion of Part II. of this research (T., 1911, 99, 649) it was shown that one coal may contain a higher percentage of "volatile matter" than another, and yet not yield so great a volume of paraffin hydrocarbons on distillation at a low temperature; and, further, that for dusts of the same degree of fineness the ease with which their inflammation was effected appeared to depend on the percentage of paraffin-yielding constituents present, and not on the percentage of volatile matter.

That there should be no relationship between the inflammabilities of different coal dusts and their contents of volatile matter, as

determined in the usual manner, is not surprising. For the determination of volatile matter simply consists in heating the coal to a high temperature and driving off all the gases that can be driven off at that temperature. Such a process can make no distinction between substances of different ease of decomposition that may be present in the coal, for it decomposes them all: nor can it offer any information regarding the proportions in which such substances may exist in different coals.

It is necessary, therefore, to obtain some means of determining the relative proportions of readily-decomposed constituents in different coals. The method employed in the paper already referred to (p. 667) was to measure the volumes of paraffins evolved per gram of the ash-free dry coals on heating them in a vacuum at 650°. A readier method lies in determining the percentages of the coals extractable by pyridine. This extraction, it is true, does not effect a complete separation of the resinous ("paraffin-yielding") from the humus ("hydrogen-yielding") constituents (see this vol., p. 1706); but, inasmuch as all that requires to be known is the *relative* proportions of the former in a number of coals, for comparison with their relative inflammabilities, complete separation is not necessary. We may, therefore, take the percentage extractable by pyridine as affording a rough measure of the relative proportions of readily-decomposed constituents in the coals experimented with. P. P. Bedson (*Trans. N.E. Min. Eng.*, **39**, 719) has already shown that the matter extracted by pyridine from a sample of coal is more readily inflammable than the coal itself.

The relative inflammability of combustible powders of like fineness depends on the relative ease with which their oxidation can be effected so as to produce flame.

In the case of coal, inflammable gases can be evolved at low temperatures. These gases consist chiefly of the paraffin hydrocarbons, the ignition-temperatures of which lie between 500° and 750°. If, therefore, coal dust be allowed to remain in contact with a surface heated to, say, 750° for a length of time sufficient to evolve a volume of paraffin hydrocarbons in excess of that required to form a "lower-limit" mixture with the surrounding air (see "The Lower Limit of Inflammation of Mixtures of the Paraffin Hydrocarbons with Air," Burgess and Wheeler, T., 1911, **99**, 2013), this mixture of gas and air should ignite, and it might, by its combustion, produce sufficient heat to cause the inflammation of an adjoining layer of dust and air mixture.

This being the case, it will be apparent that the temperature of the source of heat necessary to cause the inflammation of a particular coal dust will vary with the time of contact between the

dust-cloud and the source of heat; the temperature of inflammation will, within limits, be lower the slower the rate of passage of the cloud over the heated surface, and the greater the area of the surface (see p. 1720).

With constant conditions regarding the size of the source of heat and the time of contact of the dust particles with it, a measure of the relative inflammabilities of different dusts should be obtainable from measurements of the different temperatures to which the source of heat has to be raised in order to cause general inflammation of the dust clouds—the temperature varying with different dusts according to the ease with which the lower-limit mixture of gas and air, necessary to start the inflammation, is produced.

The production of this lower-limit mixture will depend on the composition and the volume of the gases and vapours evolved from the coal dust. The composition of the gases evolved at low temperatures from bituminous coals does not vary very much; they are mainly the paraffin hydrocarbons. There is, however, a considerable variation in the volume. At the same temperature different coals will evolve different volumes of gas; or, in other words, one coal will have to be raised to a higher temperature than another in order to produce the same amount of gas.

This being so, when seeking to determine the relative inflammabilities from measurements of the temperatures to which a given source of heat has to be raised to cause general inflammation of the dust-clouds, the size of the igniting material and the time of contact of the dust particles with it must be rendered small; otherwise there might be time enough given for the complete distillation of gas from the dusts, and such differences as are presumed in their ease of composition would be entirely masked.

The apparatus employed for determining the relative inflammabilities of different dusts is described in the experimental portion of this paper. It consisted essentially of a small source of heat, the temperature of which could be determined, over which a dust-cloud was blown at a standard speed. The relative "inflammabilities" were obtained by measuring the temperatures to which the source of heat had to be raised to cause inflammation of the dust-clouds, and are expressed as "relative ignition-temperatures."

In the table that follows the relative inflammabilities of thirty different coals (selected, on account of their low ash-content, from fifty tested) are compared with the relative proportions of resinous constituents that they contain.

Coal number.	Relative inflammabilities (expressed as ignition- temperatures under given experimental conditions).	Relative proportions of resinous constituents (expressed as percentages of the ash-free dry coal extracted by pyridine).
238	995°	38·8
250	995	37·8
227	1005	37·9
239	1005	38·2
224	1015	36·2
230	1015	35·1
214	1020	34·9
235	1020	34·4
225	1025	34·7
231	1035	28·1
206	1035	29·7
240	1045	34·4
226	1045	31·6
200	1045	29·2
229	1045	27·9
209	1045	27·2
205	1055	28·0
233	1055	26·0
208	1055	24·8
203	1055	24·7
215	1065	28·1
216	1065	26·0
218	1065	27·5
212	1065	28·7
220	1075	26·4
202	1080	26·2
219	1080	23·1
213	1090	22·1
228	1095	18·0
211	1105	20·7

It will be seen that, on the whole, the relative ignition-temperatures of the dust-clouds increase with decreasing percentages extractable by pyridine. That is to say, the lower the relative proportion of readily-decomposed constituents in the coal the lower its relative degree of inflammability.

It is not to be expected that the relationship between ignition-temperature and percentage extractable by pyridine should hold rigidly. For, as already pointed out, the pyridine extract is itself compounded of at least two types of substances, and it certainly cannot be assumed to be of unvarying composition whatever the coal from which it is obtained.

A more exact correspondence would, no doubt, be obtained between the "inflammabilities" of the coal dusts and the proportions of resinous substances that they contain as indicated by the proportions soluble in both pyridine and chloroform; but the relationship brought out by the results given above is sufficiently marked to give support to the author's view regarding the nature of "coal."

EXPERIMENTAL.

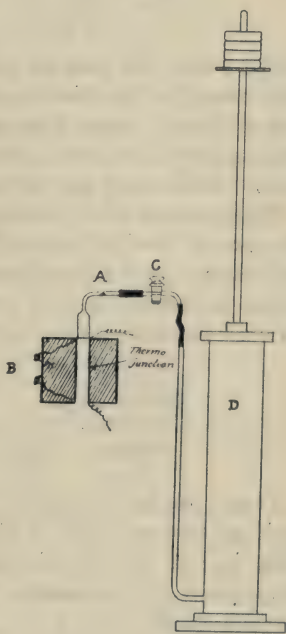
The extractions with pyridine were carried out on from 3 to 10 grams of the dried and sieved dusts in a Soxhlet fat-extraction apparatus. Some of the coals were attacked by pyridine much more rapidly than others, a dark burnt-umber colour being imparted to the liquid on contact in the cold. Such coals usually, but not always, contained a high percentage of extractive matter. Other coals gave to the pyridine a light raw-sienna colour, the solution being highly fluorescent; these coals yielded between 20 and 25 per cent. of their weight to solution in pyridine.

The Relative Inflammabilities.—For preliminary experiments regarding the influence of the area of the igniting surface and of the time of contact of the dust particles with it, on the ignition-temperature of coal dust clouds, an apparatus was employed similar to that used by J. Taffanel and A. Durr in their experiments on the inflammability of combustible dusts (*Compt. rend.*, 1911, 150, 718).

The coal dust, dried and passed through a sieve (94 meshes to the linear centimetre), was introduced into the horizontal dust-tube (A, Fig. 1), its weight being 0.2 gram. The wide portion of this dust-tube was then placed vertically over the small electric resistance furnace, B, a slip of copper gauze being introduced between the furnace tube and the dust-tube. The temperature, measured by means of a platinum and platinum-rhodium thermo-couple passing through the furnace and in contact with its walls, was regulated by an external resistance. The dust-cloud was projected downward through the furnace by quickly opening a tap (C) connecting the dust-tube to an apparatus for producing a constant puff of air. This apparatus (D) consisted of a brass cylinder about 70 cm. long and of about 10 cm. internal diameter, fitted with a piston weighted so as to give a pressure of 2 lb. per sq. in.

In order to determine the influence of the "time of contact" of the dust particles with the igniting surface on the temperature

FIG. 1.



required for ignition, a series of experiments was made in which the time of passage of the dust-cloud through the furnace was varied. This was done by altering the time of fall of the piston in the cylinder *D*. In the table that follows the relative rates of passage of the dust-clouds are given by the times taken for the piston to fall.

Time of fall of of air-piston.	Ignition-temperature of dust cloud.
2.5 secs.	940°
4.0 „	880
7.0 „	860
10.0 „	850
15.0 „	800
20.0 „	780
45.0 „	770

The slower the rate of passage of the dust-cloud through the tube the lower the ignition-temperature, no doubt because with the slower passage more time is afforded for distillation of gases from the dust, so that there is formed at a lower temperature the "lower-limit" mixture of gas and air necessary to start the inflammation.

Experiments were now made to determine the effect of increasing the area of the igniting surface. This was done by introducing into the furnace-tube a loosely-wound spiral of copper gauze, so arranged as not to restrict to any great extent the passage of the dust-cloud through the tube. The results are given in the table that follows:

Time of fall of air-piston.	Ignition temperature.	
	Furnace tube empty.	Furnace tube containing copper spiral.
12 secs.	840°	760°
35 „	820	690

These results showed clearly the influence of the area of the igniting surface, and of the time of contact of the dust particles with it, on the ignition-temperatures of coal dust clouds, and emphasised the necessity for keeping the size of the source of ignition small.

The apparatus that was finally adopted for determining the relative ignition-temperatures of the different coal dusts—thereby measuring their relative inflammabilities—is shown in Fig. 2 (p. 1715). A glass cylinder, 8 cm. in diameter and 240 cm. long, open at both ends, was supported in a horizontal position. A platinum coil of 32 gauge wire, closely wound on a thin-walled tube of quartz of capillary bore, passed horizontally across the cylinder at a point 40 cm. from one end. Through the bore of the quartz tube a platinum and platinum-rhodium thermo-couple passed. By means of suitable connexions an electric current could be passed through the platinum coil, and its temperature adjusted by an external resistance.

The dust to be tested was spread in an even layer along a glass tube of 2.5 cm. internal diameter 45 cm. long. This tube (*A*, Fig. 2) was closed at one end by a rubber stopper, carrying a glass tap, *B*, of 1 cm. bore. It was supported in the position shown in the diagram, its open end being 30 cm. from the heated platinum coil. The tap *B* was connected with the arrangement for giving a constant puff of air already described (see Fig. 1).

The platinum coil having been heated to such a temperature as preliminary trials indicated as about that required, the dust-cloud was produced by suddenly opening the tap *B*. The air-blast passing over the surface of the dust in the tube *A* raised the top layer, and carried it into the larger tube and over the heated coil in a cloud that remained uniform during the stroke of the piston. If ignition occurred, the temperature of the coil was lowered 10° and a fresh trial made, until two temperatures were obtained, differing by 10°, at one of which inflammation took place, whilst at the other the dust-cloud passed over unignited. The mean temperature was taken to be the relative temperature of ignition of the dust.

A typical photograph of the flame produced when ignition took place is reproduced in Fig. 2.

The coal dusts were obtained by pulverising nut coal, one cwt. being taken for pulverisation in each case. Their ash-content varied between 2 and 10 per cent. Since it was found (see Second Report of the Explosions in Mines Committee) that the addition of varying quantities of incombustible dust to pure coal dust altered its ignition-temperature to an appreciable extent, only those coals (thirty out of fifty experimented with) that contained less than 5 per cent. of ash are taken for comparison.

The object being to make comparison between the inflammabilities of the dusts and the composition of their coal substance, apart from adventitious moisture, ash, or "occluded" gases, each dust was dried during one hour at 107°. They were passed through a sieve (94 meshes to the linear centimetre) to bring them to the same degree of fineness.

The results of the determinations of the relative ignition-temperatures have already been given in the table on page 1718.

In the table that follows are given the ultimate and approximate analyses of the coals experimented with. The coals are arranged in the same order as on page 1718; on comparing the two tables it will be seen that there is no relationship between the relative ignition-temperatures, or "inflammabilities," and the percentages of total volatile matter in the coals.

The analyses given below were made on the sieved dusts:

Coal number.	Ultimate analysis (percentages on ash-free dry coal).					Proximate analysis (percentages).			
	C.	H.	O.	N.	S.	Moisture.	Volatile matter.	Fixed carbon.	Ash.
238	83.42	5.29	8.51	1.56	1.22	1.91	32.75	60.80	4.54
250	82.15	5.37	9.76	1.53	1.19	2.50	35.58	57.22	4.70
227	86.88	5.41	4.71	1.75	1.25	0.57	30.64	64.71	4.08
239	84.39	5.39	6.73	1.58	1.91	0.34	34.12	63.64	1.90
224	83.54	5.30	7.63	1.59	1.94	2.11	35.70	59.99	2.20
230	84.98	5.38	6.38	1.92	1.34	1.19	32.56	64.92	1.33
214	85.33	5.37	5.64	1.48	2.18	0.85	31.65	62.72	4.78
235	83.53	5.09	9.18	1.55	0.65	1.93	32.82	60.95	4.30
225	83.54	5.06	8.55	1.71	1.14	1.53	31.41	64.29	2.77
231	83.47	5.15	8.78	1.47	1.13	3.30	32.98	60.88	2.84
206	83.64	5.21	8.70	1.82	0.63	1.80	34.96	61.99	1.25
240	83.27	5.01	8.06	1.67	1.99	1.22	32.65	61.97	4.16
226	83.53	5.41	7.44	1.88	1.73	1.17	31.72	64.08	3.03
200	84.35	5.21	7.32	1.41	1.71	1.80	32.58	62.79	2.83
229	84.19	5.08	8.14	2.01	0.58	1.98	32.36	63.15	2.51
209	84.22	5.15	8.45	1.67	0.51	1.48	32.90	63.37	2.25
205	85.06	4.95	7.05	1.53	1.41	2.25	33.49	59.66	4.60
233	84.05	5.11	8.74	1.35	0.75	2.67	31.04	62.38	3.91
208	82.79	4.84	9.94	1.77	0.66	2.32	33.43	60.73	3.52
203	87.02	5.11	5.41	1.90	0.56	1.22	26.26	67.68	4.84
215	84.88	4.91	6.64	1.67	1.90	0.53	30.79	64.58	4.10
216	84.29	4.82	8.02	1.64	1.23	1.57	29.00	66.15	3.28
218	80.60	5.40	11.12	1.41	1.47	7.43	37.31	52.02	3.24
212	82.68	4.96	8.15	1.74	1.87	2.40	33.25	61.76	2.59
220	80.82	5.19	11.60	1.67	0.72	6.74	32.76	56.36	4.14
202	86.92	4.98	5.56	1.75	1.79	1.08	26.08	29.59	3.25
219	81.63	5.19	11.01	1.54	0.63	7.31	33.18	56.43	3.08
213	81.33	5.17	11.13	1.80	0.57	3.49	33.84	59.38	3.29
228	88.86	5.00	3.93	1.46	0.75	0.24	25.03	71.15	3.58
211	82.93	5.05	9.54	1.84	0.64	3.35	32.75	61.82	2.08

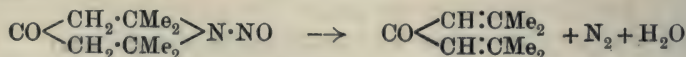
The thanks of the author are due to the Explosions in Mines Committee of the Home Office for permission to publish these results.

ESKMEALS

CLXXXV.—A New Method for the Determination of the Concentration of Hydroxyl Ions.

By FRANCIS FRANCIS and FRANK HENRY GEAKE.

In a preliminary paper by one of us and D. A. Clibbens (T., 1912, 101, 2358) it was shown that the decomposition of nitrosotriacetoneamine by alkalis into phorone and nitrogen represented as follows:



proceeded according to the first order equation. The reaction was

conveniently followed by observing the volume of nitrogen evolved, and the unimolecular equation was therefore written:

$$k = \frac{2.303}{t} \log \frac{V_{\infty} - V_0}{V_{\infty} - V},$$

where V_0 is the burette reading at the time taken as zero, V is the reading at time t , and V_{∞} the infinity reading. The results obtained with solutions of sodium hydroxide, of different concentrations, clearly indicated the possible value of the decomposition as a means for the determination of hydroxyl-ion concentration in aqueous and aqueous-alcoholic solutions up to 0.05*N* and beyond 0.3*N*.

In order to establish our view of this reaction, it was necessary to carry out a series of experiments with a variety of bases, and to determine whether the unimolecular constant was the same with those solutions of different bases containing the same concentration of hydroxyl ion.

In consequence, the catalytic decomposition of the nitrosoamine has been studied, using the following bases: Potassium hydroxide, barium hydroxide, sodium phosphate, tetramethyl- and tetraethyl-ammonium hydroxide. The results which have been obtained, and which are described in this communication, leave no doubt that the view expressed in the previous paper is correct, and that a new method has been found for the determination of hydroxyl-ion concentration within the limits previously alluded to.

A full description of the method employed will be found in the former paper (*loc. cit.*, p. 2360), and the only modification introduced consists in using a reaction flask of much smaller dimensions, namely, 100 c.c. in place of 300 c.c., thereby considerably reducing the dead space.

Following the same subdivision of the experiments described in the first paper, the results obtained with dilute solutions of bases are given in Series A, and under B those obtained with higher concentrations.

In all experiments the amount of nitrosoamine used was 0.13 gram, unless otherwise stated.

Series A 1.

Barium Hydroxide in Small Concentration.

A pure solution of this base was obtained by the method described by Ostwald-Luther, and it was found essential, when dealing with dilute solutions, to carry out the experiments in an atmosphere free from carbon dioxide. Several experiments were repeated, and it was found that the results were reproducible to within the limits

of experimental error, which is about 3 per cent. In the fourth column of table No. 1 A, the concentration of hydroxyl ions is given corresponding to that of barium hydroxide in the third column. These values have been interpolated from the measurements of A. A. Noyes on the conductivity of aqueous solutions of this base ("The Electric Conductivity of Aqueous Solutions," *Carnegie Inst. of Washington*, Publication No. 63, 1907, p. 268). The last column gives the ratio of the mean value of the velocity constant to the concentration of hydroxyl ions, and it will be seen that this ratio is constant within the limits of experimental error, and has a mean value of 1.96.

TABLE 1 A.

Expt. No.	t°	Concentration of		Constant		Mean.	k/OH'
		Ba(OH) ₂	OH'	k -minimum.	k -maximum.		
222	30.01	0.0018 <i>N</i>	0.0017 <i>N</i>	0.00322	0.00357	0.00332	1.95
226	30.00	0.0053	0.0049	0.0101	0.0109	0.0104	2.12
218	30.00	0.0077	0.0071	0.0131	0.0146	0.0137	1.93
276	30.00	0.0120	0.0108	0.0202	0.0221	0.0210	1.95
213	29.99	0.0144	0.0129	0.0250	0.0256	0.0253	1.96
211	30.07	0.0144	0.0129	0.0259	0.0266	0.0263	2.04
216	30.00	0.0181	0.0160	0.0310	0.0320	0.0314	1.96
210	30.07	0.0181	0.0160	0.0310	0.0326	0.0318	1.99
209	30.07	0.0190	0.0168	0.0345	0.0355	0.0350	2.08
239	30.00	0.0240	0.0207	0.0402	0.0405	0.0404	1.95
282	29.94	0.0412	0.0347	0.0677	0.0691	0.0684	1.97
281	30.01	0.0533	0.0440	0.0807	0.0859	0.0834	1.90
242	29.94	0.0607	0.0496	0.0884	0.0911	0.0894	1.80
241	29.94	0.064	0.0521	0.0890	0.0922	—	—
228	30.01	0.072	0.058	0.0836	0.136	—	—

In this series, out of thirty-eight experiments, seven were discarded owing to irregular results, and the mean value of the ratio k to OH' was found to be 1.96, whereas that obtained from nine experiments with dilute solutions of sodium hydroxide, described in the previous paper, was 1.82. The constancy is more clearly shown in Fig. 1, where the velocity constant has been plotted against the concentration of hydroxyl ions, and it will be noticed that the variations of the points from the straight line are almost all within 2 per cent.; the complete correspondence of the curves obtained from sodium hydroxide and barium hydroxide will also be observed. An inspection of the above table shows that the unimolecular constants commence to "drift" when a concentration of alkali has been reached approximately equal to that in the case of sodium hydroxide, where a precisely similar phenomena occurs.

SERIES A 2.

Potassium Hydroxide in Small Concentration.

Solutions of pure potassium hydroxide were prepared by a method similar to that usually employed for the preparation of sodium hydroxide, and precautions were taken against the presence of atmospheric carbon dioxide similar to those employed in the case of dilute solutions of barium hydroxide. The value for the hydroxyl-ion concentration has been taken from the source previously mentioned. The results are given in table 2 A.

TABLE 2 A.

Expt. No.	t° .	Concentration of		Constant.			k/OH' .
		KOH.	OH'.	k -minimum.	k -maximum.	Mean.	
285	29.90	0.00594 <i>N</i>	0.00575 <i>N</i>	0.00990	0.01059	0.01025	1.78
284	29.90	0.00874	0.00840	0.0162	0.0183	0.0169	2.01
286	29.90	0.0232	0.0218	0.0418	0.0439	0.0429	1.97
288	30.00	0.0289	0.0270	0.0519	0.0541	0.0531	1.96
287	29.90	0.0381	0.0353	0.0688	0.0704	0.0696	1.97
289	30.00	0.0455	0.0420	0.0777	0.0801	0.0792	1.88

The ratio of k to OH' has a mean value of 1.93, closely approximating to that obtained in the case of barium hydroxide and sodium hydroxide, and Fig. 1 clearly shows the complete correspondence existing between these three bases.

SERIES A 3.

Hydrolysis of Sodium Phosphates.

The hydrolysis of the sodium phosphates has been studied by Salm (*Zeitsch. physikal. Chem.*, 1907, **57**, 480), but the majority of the solutions he investigated were too low in hydroxyl-ion concentration to be of value for our purpose. It was found necessary to interpolate between his values for disodium hydrogen phosphate and sodium phosphate; we found on plotting the square root of the hydroxyl-ion concentration against the percentage by volume of $N/10$ -sodium phosphate in the mixture, the resulting curve approximated to a straight line between the values of pure $N/10$ -sodium phosphate and the mixture, 860 c.c. of $N/10$ -disodium hydrogen phosphate and 140 c.c. of $N/10$ -sodium phosphate. The following table 3 A shows the composition of the solutions used, together with the hydroxyl-ion concentration, either obtained direct from Salm or by interpolation in the manner described; the latter data are enclosed in square brackets.

TABLE 3 A.

Expt. No.	Volume of N/10-phosphate.			Conc. of OH'.	Constant.		
	Na_3PO_4 c.c.	Na_2HPO_4 c.c.	t°		k -minimum.	k -maximum.	Mean.
311	7	43	19.20	0.000554	0.000324	0.000356	0.000340
341	10	10	18.98	[0.0046]	0.00322	0.00363	0.00336
343	10	10	18.98	[0.0046]	0.00393	0.00451	0.00424
344	15	5	18.98	[0.00974]	0.00789	0.0869	0.00829
314	20	0	19.20	0.01852	0.0167	0.0172	0.0169
318	20	0	18.90	0.01852	0.0146	0.0154	0.0149
333	20	0	18.94	0.01852	0.0160	0.0164	0.0162

The experiments were carried out at a temperature as close to 19° as possible in order to be comparable with those given by Salm, who worked at that temperature. By means of the temperature coefficient of the reaction, the velocity constants at 30° have been calculated, and the results are given in table 4 A.

TABLE 4 A.

Expt. No.	t°	Concentration of OH'.	k at temps. given in column 2.	k calculated to 30° .	k at $30^\circ/\text{OH}'$.
311	19.20	0.000554	0.000340	0.000774	1.40
341	18.98	[0.0046]	0.00336	0.00771	1.90
343	18.98	0.0046	0.00424	0.00973	
344	18.98	[0.00974]	0.00829	0.0190	1.95
314	19.20	0.01852	0.0169	0.0385	1.98
318	18.90	0.01852	0.0149	0.0343	
333	18.94	0.01852	0.0162	0.0372	

The last column shows the ratio of k at 30° to hydroxyl ion, and it will be observed that the numbers, with the exception of experiment 311, are in close agreement with those obtained from other bases, and this agreement is made still clearer by reference to Fig. 1.

SERIES A 4.

Tetramethyl- and Tetraethyl-ammonium Hydroxides.

A few experiments described in table 5 A were carried out with these two bases, and since they are entirely different in their nature to those previously investigated, it was hardly likely that results, comparable with those obtained in the case of inorganic bases, should be obtained in these cases, were the explanation of the reaction other than that which we have advanced. The concentration of hydroxyl ions has been obtained from the results published by Bredig (*Zeitsch. physikal. Chem.*, 1894, **13**, 289).

TABLE 5 A.

Tetramethylammonium Hydroxide.

Expt. No.	<i>t</i> °.	Concentration of		Constant			<i>k</i> /OH.
		base.	OH'.	<i>k</i> -minimum.	<i>k</i> -maximum.	Mean.	
330	29.89	0.0155 <i>N</i>	0.0155 <i>N</i>	0.0288	0.0311	0.0296	1.91
329	29.89	0.0613	0.0595	0.0880	0.0941	—	—

Tetraethylammonium Hydroxide.

332	29.89	0.0155 <i>N</i>	0.0142 <i>N</i>	0.0266	0.0302	0.0288	2.03
331	29.89	0.0607	0.0537	0.0972	0.1010	0.0998	1.86

The complete correspondence between these bases and the others will be seen by reference to Fig. 1. It will be noticed further that in experiment No. 329 the unimolecular constant is "drifting," and this occurs in the same region of hydroxyl-ion concentration that has been observed in other cases.

Comparison of Data Obtained from Dilute Solutions of Alkalis.

In the following Fig. 1, the values of the velocity constants, obtained in the various experiments with different alkalis, are plotted against the hydroxyl-ion concentration. The curve shows in the most marked manner the complete agreement obtained in the velocity constant by using hydroxyl ions obtained from various sources, an agreement which, in our estimation, renders permissible the title we have used for this communication as regards solutions containing hydroxyl content up to about 0.05*N*. (The dotted curve has been drawn in Fig. 1 in order to indicate the further course of the reaction when the concentration of hydroxyl ions rises beyond 0.05*N*; the complete curve will be found in Fig. 2.

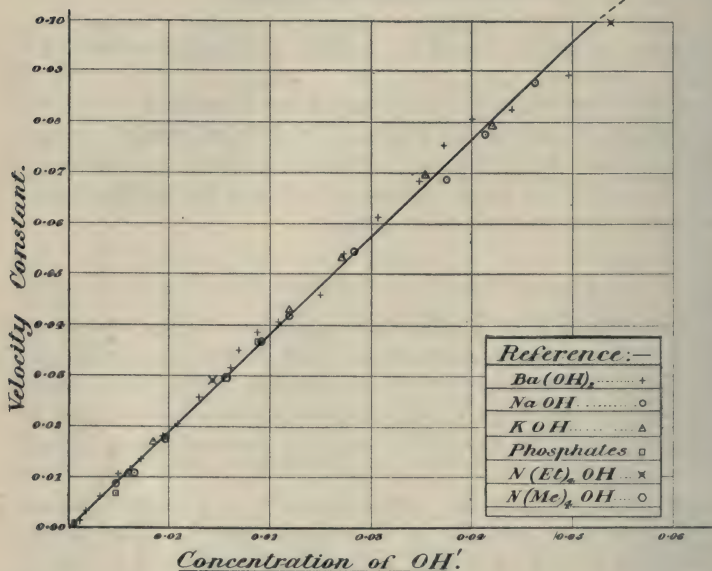
SERIES B 1.

Sodium Hydroxide in High Concentrations.

A few experiments have been previously described (*loc. cit.*, p. 2364) in which solutions of sodium hydroxide of high concentration were examined. It was observed that as the concentration of hydroxyl ions increased to about 0.05*N*, a drift in the values of the unimolecular constant became evident; this drift increased in magnitude, then became less marked, and finally ceased at a concentration of sodium hydroxide of about 0.3*N*. At the same time the velocity constant, between these two values, reached a maximum at a concentration of about 0.2*N*, and then began to fall off. A few of the thirty-five experiments carried

out with solutions of sodium hydroxide up to a concentration of this substance of about $6N$ are given in table 1 B. The corresponding concentrations of hydroxyl ions have been calculated from the conductivity data obtained by Kohlrausch (*Ann. Phys. Chem.*,

Fig.1. Relation between Velocity Constant and Concentration of Hydroxyl Ions.
Low Concentrations of OH' .



1879, [iii], 1, 1), although it is not possible to lay much stress on their accuracy, and the data have not been corrected for the possible effects of viscosity.

TABLE 1 B.

Expt. No.	t°	Concentration of		Constant.		
		NaOH.	OH'	k -minimum.	k -maximum.	Mean.
148	30.0	0.479 <i>N</i>	0.371 <i>N</i>	0.0883	0.190	0.0968
149	30.0	0.629	0.472	0.0772	0.0835	0.0794
153	29.91	0.629	0.472	0.0651	0.0781	0.0732
158	30.19	0.915	0.650	0.0547	0.0558	0.0555
160	29.90	0.915	0.650	0.0463	0.0472	0.0467
151	30.00	1.007	0.704	0.0463	0.0483	0.0473
155	29.91	1.007	0.704	0.0450	0.0474	0.0463
164	29.9	1.24	0.833	0.0357	0.0369	0.0361
172	30.0	1.24	0.833	0.0391	0.0400	0.0396
165	29.9	1.48	0.956	0.0274	0.0289	0.0284

TABLE 1 B (*continued*).

Expt. No.	t° .	Concentration of		Constant.		
		NaOH.	OH'.	k -minimum.	k -maximum.	Mean.
167	29.9	1.93 <i>N</i>	1.139 <i>N</i>	0.0208	0.0216	0.0212
175	30.0	1.93	1.139	0.0194	0.0205	0.0199
177	30.08	2.62	1.341	0.0129	0.0147	0.0138
170	30.0	2.97	1.416	0.0119	0.0128	0.0121
184	30.0	3.30	1.464	0.0114	0.0124	0.0120
171	30.0	3.72	1.514	0.0102	0.0111	0.0106
188	29.9	4.12	1.538	0.0099	0.0107	0.0101
196	30.19	4.19	1.548	0.0099	0.0132	0.0115
191	29.9	5.70	1.482	0.00911	0.0124	0.0103

The above table clearly shows that as the concentration of sodium hydroxide rises, the rate of reaction diminishes, and at concentrations beyond 3.5*N* becomes almost constant, and about equal to that given by dilute solutions of concentration 0.005*N*. This is shown still more clearly in Fig. 2, obtained by plotting the velocity constant against the concentration of hydroxyl ions. The curve falls rapidly at first, but as the concentration increases, the slope becomes less, until at about 3.5*N*-sodium hydroxide, corresponding with an hydroxyl-ion concentration of about 1.5*N*, it is practically horizontal. Unlike the previous curves, it will be seen that it is no longer a straight line, but approximates to a hyperbola, that is, the rate of reaction has ceased to be inversely proportional to the first power of the concentration of hydroxyl ions.

SERIES B 2.

Potassium Hydroxide in High Concentrations.

The results obtained with solutions of potassium hydroxide are given in table 2 B, where the concentration of hydroxyl ions corresponding with that of the base has been calculated from the measurements of Kohlrausch of the conductivity of strong solutions.

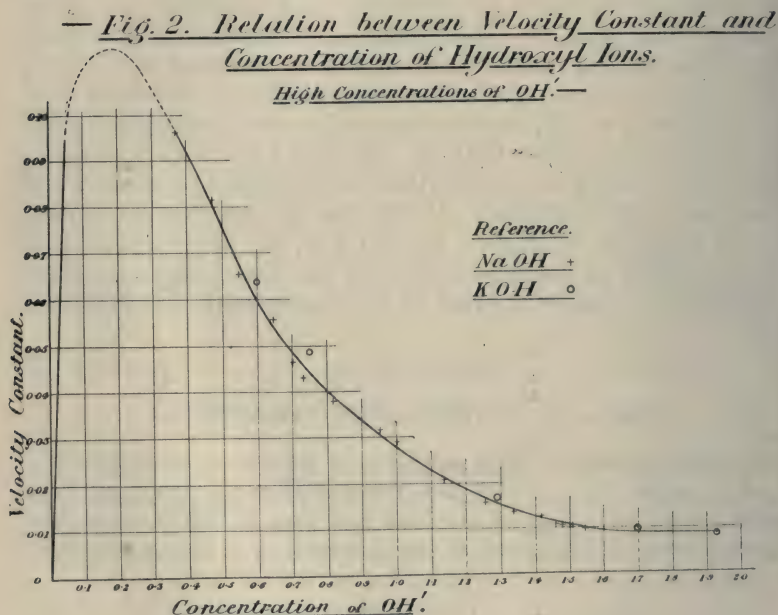
TABLE 2 B.

Expt. No.	t° .	Concentration of		Constant.		Mean.
		KOH.	OH'.	k -minimum.	k -maximum.	
290	30.00	0.107 <i>N</i>	0.0957 <i>N</i>	0.108	0.146	—
291	30.00	0.197	0.170	0.111	0.163	—
292	29.94	0.275	0.236	0.0981	0.143	—
293	29.94	0.433	0.362	0.0949	0.109	—
294	29.94	0.757	0.600	0.0629	0.0652	0.0639
299	30.12	0.967	0.751	0.0475	0.0489	0.0484
300	30.12	1.88	1.294	0.0162	0.0175	0.0167
327	30.12	2.80	1.696	0.00893	0.00976	0.00947
302	30.12	3.51	1.932	0.00802	0.00878	0.00846

The striking similarity between potassium and sodium hydroxides, previously shown in the case of dilute solutions, is equally marked as the concentration of alkali rises; the "drift" in the unimolecular constants of each commences at the same concentration; the constant reaches a maximum in both cases when the concentration of hydroxyl is in the neighbourhood of $0.2N$, falls in a similar manner in each case, and the "drift" ceases at a concentration of hydroxyl approximately the same for each substance..

Comparison of Data Obtained from Concentrated Solutions of Alkalis.

A comparison of the behaviour of the two substances sodium and potassium hydroxide is shown in Fig. 2, where the velocity constants



have been plotted against the concentration of hydroxyl ions. (The first part of the curve is that given in Fig. 1, where it will be noticed that the scale is much larger, but it has been drawn here in order that a complete picture of the course of the reaction may be obtained, that is, the catalysis of the decomposition of nitrosotriacetone under the influence of small and high concentrations of hydroxyl ions.)

The two curves for concentrated solutions are similar in shape,

and nearly coincide, but since in such solutions potassium hydroxide is much more highly dissociated than sodium hydroxide, it has been found possible in the case of the former base to follow the curve into higher concentrations of hydroxyl ions.

The Influence of Neutral Salts.

A few experiments were carried out in the presence of neutral salts in order to determine whether the velocity constant was affected in any way. The salts employed were sodium chloride, nitrate, sulphate, and acetate, and the results obtained are described in table No. 2.

It will be seen that neutral salts in moderate concentration have practically no influence on the velocity constant.

When, however, the concentration of such salts was high, a marked decrease in the magnitude of the constants was observed in dilute solutions of hydroxyl ions, and, on the other hand, a distinct increase in the value of these constants in more concentrated solutions of such ions. This will be seen on reference to table 2, Nos. A and B respectively. When it is remembered that in such high concentration of neutral salts the effect on the degree of dissociation of the base is considerable, it will be seen that the essential effects of neutral salts on the velocity constant, both in the case of low and high concentration of hydroxyl ions, may be ascribed to the effect of such salts in driving back the dissociation of the alkali.

This explanation appears to be borne out by the effects produced by sodium salts on potassium hydroxide, table 2 No. C; in such concentrations of alkali the reaction is accelerated because the sodium hydroxide formed is less dissociated than the corresponding potassium compound.

We propose, however, to investigate the action of neutral salts more completely, and reserve for a future communication the bearing of these results on the hypothesis of the hydration of salts in solution.

TABLE 2.

No. A.

Expt. No.	t° .	Concentration of		Mean value of k .
		alkali.	neutral salt.	
348	29.81	0.026 <i>N</i> -NaOH	—	0.0407
345	29.81	0.026 <i>N</i> -NaOH	6 <i>N</i> -NaNO ₃	0.00713
346	29.81	0.026 <i>N</i> -NaOH	4 <i>N</i> -NaNO ₃	0.0110
347	29.81	0.026 <i>N</i> -NaOH	3 <i>N</i> -NaNO ₃	0.0140
349	30.02	0.026 <i>N</i> -NaOH	2 <i>N</i> -NaNO ₃	0.0207
350	30.02	0.026 <i>N</i> -NaOH	1 <i>N</i> -NaNO ₃	0.0260
351	30.02	0.026 <i>N</i> -NaOH	1 <i>N</i> -Na ₂ SO ₄	0.0410

TABLE 2. No. A (*continued*).

Expt. No.	<i>t</i> °.	Concentration of		Mean value of <i>k</i> .
		alkali.	neutral salt.	
352	30.02	0.026 <i>N</i> -NaOH	2 <i>N</i> -Na ₂ SO ₄	0.0322
135	30.20	0.027 <i>N</i> -NaOH	—	0.0523
132	30.20	0.027 <i>N</i> -NaOH	0.019 <i>N</i> -NaCl	0.0510
133	30.20	0.027 <i>N</i> -NaOH	0.019 <i>N</i> -NaNO ₃	0.0524
134	30.20	0.027 <i>N</i> -NaOH	0.019 <i>N</i> -Na ₂ SO ₄	0.0534
139	29.97	0.04 <i>N</i> -NaOH	—	0.0625
136	29.97	0.04 <i>N</i> -NaOH	0.04 <i>N</i> -NaCl	0.0641
137	29.97	0.04 <i>N</i> -NaOH	0.04 <i>N</i> -NaNO ₃	0.0507
138	29.97	0.04 <i>N</i> -NaOH	0.04 <i>N</i> -Na ₂ SO ₄	0.0541
131	30.19	0.0518 <i>N</i> -NaOH	—	0.0752
128	30.19	0.0518 <i>N</i> -NaOH	0.0182 <i>N</i> -NaCl	0.0793
129	30.19	0.0518 <i>N</i> -NaOH	0.0182 <i>N</i> -NaNO ₃	0.0766

No. B.

127	30.3	0.26 <i>N</i> -NaOH	—	0.129
124	30.3	0.26 <i>N</i> -NaOH	0.0182 <i>N</i> -NaCl	0.124
126	30.3	0.26 <i>N</i> -NaOH	0.0182 <i>N</i> -NaNO ₃	0.144
147	30.01	1.0 <i>N</i> -NaOH	—	0.0478
142	29.78	1.0 <i>N</i> -NaOH	1.0 <i>N</i> -Na ₂ SO ₄	0.0512
145	30.01	1.0 <i>N</i> -NaOH	4.0 <i>N</i> -NaNO ₃	0.0560
146	30.01	1.0 <i>N</i> -NaOH	1.0 <i>N</i> -NaAc	0.0459

No. C.

306	30.19	0.967 <i>N</i> -KOH	—	0.0443
303	30.19	0.967 <i>N</i> -KOH	1.00 <i>N</i> -NaCl	0.0481
304	30.19	0.967 <i>N</i> -KOH	1.00 <i>N</i> -NaNO ₃	0.0473
305	30.19	0.967 <i>N</i> -KOH	1.00 <i>N</i> -NaAc	0.0522

Temperature-coefficient.

A few experiments on the determination of this coefficient have been previously described (*loc. cit.*, p. 2370), but it was pointed out that no great stress could be laid on the values obtained, namely, 3.18 and 3.17.

In order to determine this coefficient with a greater degree of accuracy, a series of experiments were carried out at a temperature of about 40°, and some of the results obtained are given in table 3. Under *k_c* are given the mean value of the velocity constant obtained by experiments at temperatures given in the second column, and these are compared under *k_{30°}* with the values obtained from the same concentration of alkali at 30°. These values were calculated from the hydroxyl-ion concentration by using the mean value of the ratio *k*/OH' = 1.96. In the last column, the temperature-coefficient has been worked out for each individual experiment, and the values obtained agree within about 6.4 per cent. The mean value from nineteen determinations is 2.17.

Another method of calculating the coefficient, and one which avoids the error due to the fact that the temperatures of the experiments range over more than 1°, consists in comparing the

slope of the curve obtained by plotting the value of the velocity constants obtained at 40° against the corresponding hydroxyl-ion concentration with that similarly obtained for values at 30° . This treatment gives a value of 2.24, hence the mean value of the temperature-coefficient may be taken as 2.20.

TABLE 3.

Expt. No.	t° .	Concentration of		k_{40} .	k_{30} .	Temp.- coefficient.
		alkali.	OH'.			
245	39.90	0.0066 <i>N</i>	0.00596 <i>N</i>	0.0224	0.0116	1.923
249	39.79	0.0066	0.00596	0.0248	0.0116	2.117
250	39.79	0.0103	0.00915	0.0426	0.0179	2.357
261	39.10	0.0190	0.0184	0.0825	0.0360	2.198
260	39.10	0.0221	0.0213	0.0970	0.0417	2.231
257	38.70	0.0426	0.0406	0.166	0.0795	1.962
265	39.28	0.0426	0.0406	0.173	0.0795	2.105
256	38.70	0.0507	0.0482	0.207	0.0943	2.063

Conclusion.

We are still unable to offer any further suggestions in explanation of the peculiar quantitative results described in this and the previous communication. We are at present engaged in a study of the conductivity of solutions of nitrosotriacetoneamine and of such solutions in the presence of alkali, and it is possible that the results of this investigation may throw some light on the mechanism of the decomposition.

We have no doubt, however, that the views expressed in the previous communication are correct, namely, that the nitrosoamine is catalytically decomposed into phorone and nitrogen under the influence of hydroxyl ions, and that the rate of this reaction is proportional to the concentration of these ions up to that of 0.05*N*. It appears to us very significant that the velocity constants determined in the presence of aqueous solutions of sodium, potassium, and barium hydroxides are not proportional to the concentration of the bases themselves, but in all three cases are very nearly proportional to the concentration of the hydroxyl ions as deduced from conductivity measurements. Moreover, in the cases previously discussed, when comparison between different bases is possible, it has been found that the drift in the unimolecular constants sets in at about the same concentration of hydroxyl ions; that in the case of sodium and potassium hydroxides the reaction velocity reaches a maximum at the same concentration of hydroxyl ions; the drift in these constants ceases at the same concentration, and the subsequent curves for both bases nearly coincide.

Reference to table 1 B, experiments 170 to 191, shows that the velocity constant varies but little between concentrations of sodium hydroxide of 2.97*N* to 5.7*N*, clearly indicating that this constant is

parallel, not to the concentration of that base which is nearly doubled, but to that of the hydroxyl-ion concentration, which alters but slightly between these two points.

Finally, a higher concentration of hydroxyl ions can be obtained with potassium hydroxide owing to the fact that this base is dissociated, in such concentrations, to a much greater extent than is sodium hydroxide, and again, table 2 B, experiments 327, 302, shows that the velocity constant is parallel with this increased concentration. We do not consider that such behaviour would be expected were the explanation other than that which we have advanced.

We are confirmed in our views by the agreement in the values obtained from the hydroxyl-ion concentration in solutions of the sodium phosphates and the two organic bases.

The importance of the method, as a means for the determination of hydroxyl-ion concentration, lies in the fact that the effects of neutral salts in ordinary concentrations is unimportant.

A survey of the data obtained shows that in any individual experiment the values of the velocity constant agree to within 1—2 per cent., and that the results are reproducible to within 2—3 per cent.

The method is consequently available for the estimation of the concentration of hydroxyl ions to this degree of accuracy up to 0.05*N*-hydroxyl ion, and the general formula may be expressed as follows:

$$\text{Concentration of OH}' = k_p/R,$$

where $R = 1.96 \times 2.20 \frac{t^\circ - 30}{10}$.

k_p is the observed constant at the temperature t° , and R is the ratio between k_{t° and the value of the OH'-ion for the temperature t° . $R = 0.184$ at 0° ; 0.601 at 15° ; 0.891 at 20° ; 1.32 at 25° ; 1.96 at 30° ; and 4.31 at 40° .

Between concentrations of 0.05*N* and 0.3*N*-hydroxyl ion the unimolecular constants "drift," and the method is consequently inapplicable for the determination of the concentration of hydroxyl ions within these limits. The drift ceases, however, at the latter concentration, and from that point up to 1.4*N* the accuracy is diminished, and beyond this, considerably diminished, since the velocity constants only change slightly with large increases in the concentration of hydroxyl ions. The most satisfactory method of dealing with such high concentrations is by interpolation on the curve of standard results described above.

CLXXXVI.—*The Methylation of Cellulose.*

By WILLIAM SMITH DENHAM and HILDA WOODHOUSE (Carnegie Scholar).

THE correctness of the view, which has been long maintained, that the cellulose molecule is composed wholly of dextrose residues, seems now to have been established definitely by the work of Willstätter and Zechmeister (*Ber.*, 1913, **46**, 2401), who, using concentrated aqueous hydrochloric acid as the hydrolytic agent, have effected the quantitative conversion of cellulose into dextrose. The high yields of the acetates of dextrose and cellulose obtained by the acetolytic method of degradation point to the same conclusion (Ost, *Annalen*, 1913, **398**, 342). Whilst further study of the products of acetolysis may yield an insight into the manner of linking of the dextrose residues in these derivatives, and therefore in the parent substance, another method of attack on the problem of the constitution of the polysaccharides is suggested by the results of the investigations, still in progress, of Irvine and his collaborators on the constitution of the methylated monosaccharides. If cellulose, for example, were methylated, subsequent cleavage of the molecule should yield one or more of the methylated dextroses in which the methoxyl groups represent hydroxyl groups of the original cellulose complex, so that the nature of the linkings would be determined to an extent dependent on the degree to which the cellulose had been methylated before the cleavage of the molecule.

As a first step in this direction the authors attempted various methods of methylating cellulose, and found that the methylation can be effected very simply by the action of methyl sulphate on the fibrous substance after it has been impregnated with a 15 per cent. solution of sodium hydroxide. Under the conditions adopted, the reaction appears to proceed in definite stages; thus, notwithstanding the presence of sodium hydroxide in somewhat greater quantity than that represented by the ratio $C_6H_{10}O_5 : 2NaOH$ and of excess of methyl sulphate over that required for the alkali, the composition of the product is that of a substance of the empirical formula $C_{12}H_{19}O_9 \cdot OMe$. If the treatment with sodium hydroxide and methyl sulphate is repeated, the new product has the composition given by the formula $C_6H_9O_4 \cdot OMe$, whilst the substance produced on a third treatment is most nearly represented by the less simple formula $C_{24}H_{35}O_{15}(OMe)_5$. Similar results have been obtained in several series of experiments. The material has not yet been subjected to a fourth treatment. Although the products at the different stages can be adequately represented by such simple

empirical formulæ, and some basis for speculation regarding the relative activity of the different hydrogen atoms in the cellulose molecule is therefore afforded by the gradation thus indicated in the methylation, such discussion would be premature until the homogeneity of the various products is more definitely established.

The methylated celluloses retain the fibrous structure of the original material, but with increasing degree of methylation the dried substance becomes more and more horny in appearance. The first product, $C_{12}H_{19}O_9 \cdot OMe$, is readily dissolved by the cuprammonium solvent, the others less readily. Apparently only the first product dissolves in a solution of zinc chloride in hydrochloric acid. They can all be acetylated. That the methoxyl group exists in a state of combination is shown by the high temperature ($120-130^\circ$) to which they must be heated with hydriodic acid during the methoxyl determination by Zeisel's method before a precipitate forms in the silver nitrate solution, and the fact is further established by the persistence of the methoxyl group during subsequent reactions.

The first product, $C_{12}H_{19}O_9 \cdot OMe$, undergoes a slight change in composition when it is treated with a 15 per cent. solution of sodium hydroxide alone, the recovered substance (which is less in weight) showing a diminished percentage of carbon, hydrogen, and, possibly, of methoxyl.

The product from the second methylation, $C_6H_9O_4 \cdot OMe$, can be converted into a xanthate by treatment with sodium hydroxide solution and carbon disulphide in a manner similar to that in which viscose is prepared from ordinary cellulose. The methylated cellulose regenerated from the filtered solution by warming it on the water-bath contains slightly less methoxyl than the original substance. The formation of this methylated viscose is of interest in relation to the question of the relative reactivity of the hydrogen atoms of cellulose, for, if the most reactive hydrogen atom of the unit, $C_6H_{10}O_5$, is replaced in ordinary viscose from cellulose by the $\cdot CS \cdot SNa$ group, and in the methylated cellulose by the methyl group, it is evident (if the compositions of the xanthates are similar) that the xanthate from ordinary cellulose must involve in its formation a different hydrogen atom from that which is concerned in the formation of the xanthate from the methylated cellulose.

The methylated celluloses, when acted on by a mixture of acetic anhydride and acetic acid which contains a trace of sulphuric acid, give acetyl derivatives, which are readily soluble in chloroform, and show some resemblance to acetyl cellulose. Analyses of the products, however, show that they contain less carbon, hydrogen, and methoxyl than would be present in completely acetylated derivatives

of the methylated celluloses, but the analytical figures do not favour the view that acetylation is incomplete. They indicate that partial elimination of the methoxyl group has occurred—accompanied perhaps by degradation of the molecule with consequent greater degree of acetylation than if there were no such change. Two of the analysed samples showed signs of decomposition.

EXPERIMENTAL.

The cellulose used in the following experiments was (1) calico—a sample of “madder” bleached calico kindly supplied by Mr. W. E. Kay, of the Calico Printers’ Association, similar to that described by Cross (“Researches on Cellulose,” III., p. 22, No. 1) as a typical “normal” cellulose—and (2) ordinary cotton-wool. The calico was cut up very finely and beaten under water so as to disintegrate the fibre as far as possible, but it still contained some pieces of fabric after this treatment.

The treatment to which the cellulose was subjected is (with minor variations) as follows: Alkali-cellulose was prepared by leaving the cotton for one or more days in contact with three to four times its weight of 15–17 per cent. solution of sodium hydroxide. The proportions of cellulose to sodium hydroxide were therefore approximately $\text{C}_6\text{H}_{10}\text{O}_5 : 2\text{NaOH}$, but a slightly greater quantity of sodium hydroxide was usually present. On addition of the amount of methyl sulphate required to react with the sodium hydroxide, reaction occurs with evolution of heat, but when the mixture cools it is still alkaline, and remains so obstinately even on gentle warming, unless a considerable excess of methyl sulphate is added. The product was washed repeatedly by decantation with distilled water, then with very dilute alkali and acid successively, and finally with water again. The process of washing is tedious, but was carried out very thoroughly, especially in the portions used for analysis. The analysed material was dried in a vacuum at about 120° until constant in weight. The subsequent treatments with sodium hydroxide and methyl sulphate were carried out similarly. It was not practicable to determine the yields when calico was used, owing to the presence of particles of fabric which were less completely methylated than the loose fibres, but the yields of the products from cotton-wool were determined.

First Treatment.

(A) *Calico*.—Fifty grams of the disintegrated material which had been dried at 100° were soaked in 200 c.c. of 15 per cent. solution of sodium hydroxide, and the mixture was allowed to remain for

three days with frequent stirring. Fifty-two grams of methyl sulphate were then added instead of the 45 grams required to react with the sodium hydroxide present. When the heat of reaction had subsided, the mixture remained alkaline, even on gentle warming. An additional quantity of 10 grams of methyl sulphate was therefore added, and the mixture was shaken with 500 c.c. of benzene, but it was still alkaline three days later, and when neutralised with hydrochloric acid required the equivalent of 8 grams of sodium hydroxide for neutralisation. It is inadvisable to use benzene as a solvent for the methyl sulphate, since a persistent emulsion is formed; in subsequent experiments a large excess of methyl sulphate was used instead. The portions of the product which still showed the structure of the fabric were separated from the fibres.

Fabric:

0.2975 gave 0.1043 AgI. $\text{OMe}=4.63$.

Fibres:

0.1212 gave 0.2034 CO_2 and 0.0706 H_2O . $\text{C}=45.77$; $\text{H}=6.47$.

0.3064 „ 0.2350 AgI. $\text{OMe}=10.14$.

$\text{C}_{12}\text{H}_{19}\text{O}_9 \cdot \text{OMe}$ requires $\text{C}=46.15$; $\text{H}=6.51$; $\text{OMe}=9.29$ per cent.

(B) *Cotton-wool*.—Eighty grams of cotton-wool (dried in the steam-oven), after remaining for three days with 250 c.c. of 15 per cent. solution of sodium hydroxide, were treated with 145 grams of methyl sulphate (two and a-half times the theoretical quantity calculated on the sodium hydroxide), when much heat was evolved. The yield of the washed and dried product was 90 per cent. of the calculated amount; there was, of course, some unavoidable loss in washing:

0.1674 gave 0.2819 CO_2 and 0.0964 H_2O . $\text{C}=45.93$; $\text{H}=6.40$.

0.2782 „ 0.1791 AgI. $\text{OMe}=8.5$.

$\text{C}_{12}\text{H}_{19}\text{O}_9 \cdot \text{OMe}$ requires $\text{C}=46.15$; $\text{H}=6.51$; $\text{OMe}=9.29$ per cent.

Second Treatment.

(A) *Calico*.—Forty-three grams of the crude product from the first treatment were allowed to stand for one and a-half days with 170 c.c. of 15 per cent. solution of sodium hydroxide. The calculated quantity of methyl sulphate (reckoned on the sodium hydroxide) was then added, and the mixture was thoroughly stirred. After more than three weeks the mixture was still alkaline; it was therefore neutralised with hydrochloric acid, and, after washing with water, the pieces of fabric were separated from the loose fibres.

Fabric:

0.3314 gave 0.1777 AgI. $\text{OMe}=7.08$.

Fibres:

0.1338 gave 0.2330 CO_2 and 0.0826 H_2O . $\text{C}=47.49$; $\text{H}=6.86$.

0.3189 „ 0.4046 AgI . $\text{OMe}=16.77$.

$\text{C}_6\text{H}_9\text{O}_4\cdot\text{OMe}$ requires $\text{C}=47.72$; $\text{H}=6.82$; $\text{OMe}=17.62$ per cent.

(B) *Cotton-wool*.—This preparation was carried out similarly to the above, except that one and a-half times the calculated quantity of methyl sulphate was used. After remaining overnight, the mixture was still alkaline, but was rendered acid in reaction by the addition of another equivalent of methyl sulphate. The yield was 80 per cent. of the calculated amount:

0.1640 gave 0.2895 CO_2 and 0.1015 H_2O . $\text{C}=48.14$; $\text{H}=6.88$.

0.3466 „ 0.5176 AgI . $\text{OMe}=19.72$.

$\text{C}_6\text{H}_9\text{O}_4\cdot\text{OMe}$ requires $\text{C}=47.72$; $\text{H}=6.82$; $\text{OMe}=17.62$ per cent.

Third Treatment.

(A) *Calico*.—The loose fibres only were treated further. These when dry formed a horny mass, which was penetrated by the sodium hydroxide solution with difficulty. Two distinct preparations were carried out, the quantities used being in (1) 12 grams of the twice methylated substance, 33 c.c. of 17 per cent. solution of sodium hydroxide and 30 grams of methyl sulphate, and in (2) 2 grams of the twice methylated substance, 8 c.c. of 15 per cent. solution of sodium hydroxide and 12 grams of methyl sulphate:

(1) 0.1810 gave 0.3122 CO_2 and 0.1100 H_2O . $\text{C}=47.04$; $\text{H}=6.75$.

0.1600 „ 0.2782 CO_2 „ 0.0979 H_2O . $\text{C}=47.42$; $\text{H}=6.80$.

0.2645 „ 0.4310 AgI . $\text{OMe}=21.53$.

(2) 0.1359 „ 0.2409 CO_2 and 0.0845 H_2O . $\text{C}=48.34$; $\text{H}=6.91$.

0.3056 „ 0.5114 AgI . $\text{OMe}=22.11$.

$\text{C}_{24}\text{H}_{35}\text{O}_{15}(\text{OMe})_5$ requires $\text{C}=48.47$; $\text{H}=6.96$; $\text{OMe}=21.59$ per cent.

(B) *Cotton-wool*.—Twenty grams of the twice methylated substance, after remaining for two days in contact with 54 c.c. of 17 per cent. solution of sodium hydroxide, were treated with 11 grams of methyl sulphate. The yield was 73 per cent. of the calculated amount:

0.1892 gave 0.3355 CO_2 and 0.1223 H_2O . $\text{C}=48.36$; $\text{H}=7.18$.

0.2799 „ 0.5760 AgI . $\text{OMe}=23.3$.

$\text{C}_{24}\text{H}_{35}\text{O}_{15}(\text{OMe})_5$ requires $\text{C}=48.47$; $\text{H}=6.96$; $\text{OMe}=21.59$ per cent.

*Action of Sodium Hydroxide on the Product from the First
Methylation of Cotton-wool.*

Two grams of the methylated product, dried at 100° , were allowed to remain for four days in contact with 8 c.c. of 15 per cent. solution

of sodium hydroxide. After washing with water and drying, the substance weighed 1.68 grams:

0.1430 gave 0.2382 CO_2 and 0.1430 H_2O . $\text{C}=45.43$; $\text{H}=6.29$.

0.1680 „ 0.2780 CO_2 „ 0.1017 H_2O . $\text{C}=45.13$; $\text{H}=6.01$.

0.1715 „ 0.1013 AgI . $\text{OMe}=7.8$.

The composition before treatment was: $\text{C}=45.83$; $\text{H}=6.44$; $\text{OMe}=8.5$. The washings after concentration on the water-bath were found to reduce Fehling's solution.

Conversion of the Twice Methylated Product from Cotton-wool into a Xanthate.—Regeneration of the Methylated Cellulose.

Eight grams of carbon disulphide were added to a mixture of 10 grams of the methylated cellulose and 30 grams of an 18 per cent. solution of sodium hydroxide which had been in contact with each other for twenty-four hours, and the whole was allowed to remain for six hours in a stoppered bottle with frequent stirring. After exposure to the air for a few minutes to remove any excess of carbon disulphide, the mass was brought into solution by prolonged stirring with 30 c.c. of an 18 per cent. solution of sodium hydroxide. The solution after dilution with about 2 litres of water was filtered through nickel gauze, and finally through filter paper—a slow process owing to the presence of undissolved gelatinous matter. The methyl cellulose regenerated by heating the solution on the water-bath was washed by decantation with large quantities of water. In a second experiment the procedure was similar, except that 90 c.c. of the sodium hydroxide solution were used to dissolve the reaction product:

I. 0.2659 gave 0.2834 AgI . $\text{OMe}=14.08$.

II. 0.2046 „ 0.2423 AgI . $\text{OMe}=15.64$.

The methylated cellulose used contained $\text{OMe}=19.72$ per cent.

Acetylation of the Methylated Celluloses derived from Cotton-wool.

The procedure was similar in each case; 2 grams of the methylated cellulose were treated with a mixture of 8 grams of acetic anhydride, 8 grams of acetic acid, and a trace of sulphuric acid. The mass was stirred continuously for an hour, the temperature being kept below 30° . After the mixture had remained for about twelve hours at the ordinary temperature with occasional stirring, it was warmed to 35° for a few minutes, then diluted with acetic acid, and filtered through a perforated plate to remove the small quantity of undissolved matter. The acetyl compound was precipitated by pouring the solution into water, and was washed with water until the

particles had no longer an acid reaction. The film deposited on the evaporation of a chloroform solution was analysed after it had been dried in a vacuum at about 90° until the weight was constant. The films of the substances numbered I and II below were coloured, evidently owing to slight decomposition; that from substance III was colourless. The acetic acid was determined by dissolving the acetyl compound in a mixture of equal volumes of sulphuric acid and water and subsequent distillation with steam. From the alkali required for the distillate during the first four hours was deducted that required for the second four hours' distillate, which was taken to represent the amount required to neutralise the volatile acid derived from the decomposition of the molecule assumed constant throughout (Schliemann, *Annalen*, 1911, **378**, 368). Substance I required 14.66 c.c. $N/2$ -NaOH for the first period and 3.52 c.c. $N/2$ -NaOH for the second period; for substance II the quantities of $N/2$ -NaOH required were 12.30 c.c. and 3.36 c.c. With substance III the method failed as the amount of alkali required was the same for each period. The results for substances I and II may therefore be untrustworthy.

I. Acetyl Derivative from the First Methylation Product.

0.1802 gave 0.3026 CO_2 and 0.0869 H_2O . $\text{C}=45.79$; $\text{H}=5.36$.
 0.3560 „ 0.1070 AgI. $\text{OMe}=3.97$.
 0.6066 „ 0.3342 $\text{C}_2\text{H}_4\text{O}_2$. $\text{C}_2\text{H}_4\text{O}_2=55.09$.
 $\text{C}_{12}\text{H}_{14}(\text{CH}_3\cdot\text{CO})_5\text{O}_9\cdot\text{OMe}$ requires $\text{C}=50.36$; $\text{H}=5.84$; $\text{OMe}=5.66$;
 $\text{C}_2\text{H}_4\text{O}_2=54.74$ per cent.

II. Acetyl Derivative from the Second Methylation Product.

0.1461 gave 0.2467 CO_2 and 0.0712 H_2O . $\text{C}=46.05$; $\text{H}=5.38$.
 0.3202 „ 0.1469 AgI. $\text{OMe}=6.06$.
 0.5025 „ 0.2682 $\text{C}_2\text{H}_4\text{O}_2$. $\text{C}_2\text{H}_4\text{O}_2=53.43$.
 $\text{C}_6\text{H}_7(\text{CH}_3\cdot\text{CO})_2\text{O}_4\cdot\text{OMe}$ requires $\text{C}=50.97$; $\text{H}=6.02$; $\text{OMe}=11.29$;
 $\text{C}_2\text{H}_4\text{O}_2=46.15$ per cent.

III. Acetyl Derivative from the Third Methylation Product.

0.1954 gave 0.3460 CO_2 and 0.1024 H_2O . $\text{C}=48.29$; $\text{C}=5.83$.
 0.2954 „ 0.2800 AgI. $\text{OMe}=12.7$.
 $\text{C}_{24}\text{H}_{28}(\text{CH}_3\cdot\text{CO})_7\text{O}_{15}(\text{OMe})_5$ requires $\text{C}=50.99$; $\text{H}=6.31$;
 $\text{OMe}=15.32$ per cent.*

* During the progress of this work, and after most of the results just recapitulated had been reported to the Carnegie Trust, an abstract of a patent dealing with similar problem was published (*J. Soc. Chem. Ind.*, 1913, **32**, 420). In the full specification (French Patent 447,974, published 20th January, 1913)

The authors desire to express their thanks to Professor Irvine for the helpful interest he has taken in this work, and to the Carnegie Trust for its contribution to the cost.

CHEMICAL RESEARCH LABORATORY,
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS.

THE Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society :

WHINFIELD,
SALCOMBE,
S. DEVON.
Sept. 16th, 1913.

GENTLEMEN,

I have the honour to forward the Annual Report of the International Committee on Atomic Weights for 1914, which is submitted for publication in the Society's Transactions and Proceedings, as hitherto.

The Report deals with all the determinations of atomic weights which have been published since the issue of the preceding Report, but, in accordance with the resolution passed at the Eighth International Congress of Applied Chemistry, it is not proposed to make any change in the official table of atomic weights until the meeting of the next Congress in 1915.

Apart from this, the work of the past year has not shown any necessity for any addition to the existing list of Atomic Weights, or for any substantial alteration in the values last published.

Lilienfeld describes the preparation of cellulose ethers (ethyl celluloses) by the action of ethyl sulphate on solutions of regenerated cellulose in concentrated sodium hydroxide solution. It is stated that substances of various degrees of ethylation can be prepared and that the products are soluble in organic solvents or in some cases even in water ; analytical figures (for carbon and hydrogen) are given for a substance of the composition $C_{12}H_{15}O_5(OEt)_5$. The manner of preparation of these substances and their range of solubility suggest that the cellulose molecule has undergone considerable degradation. The authors, on the other hand, have endeavoured to carry out the methylation with as little alteration as possible of the cellulose complex, and it is their intention to continue the investigation of the progressive methylation of cellulose and to study the cleavage products obtainable from the methylated celluloses.

Experiments conducted on lines similar to those described above have also been carried out by the authors on starch, the results showing that the starch molecule similarly undergoes normal methylation.

It is accordingly recommended that the table accompanying the Report for 1913 should be reprinted as it stands.

I have appended the signatures of Professors Ostwald and Urbain as desired by them.

I am, Gentlemen,

Your obedient Servant,

T. E. THORPE.

*The Hon. Secretaries,
The Chemical Society,
London.*

Annual Report of the International Committee on Atomic Weights, 1914.

At the Eighth International Congress of Applied Chemistry, held in New York in September, 1912, a resolution was passed favouring less frequent changes in the official table of atomic weights. Such changes are sometimes embarrassing to technical chemists, and the resolution adopted expressed a desire that the table for 1913 should remain, for legal and commercial use, the official table until the next Congress convenes, in 1915. With this wish the Committee can easily comply; at least, in its essential features, for changes which affect the industrial chemist are not likely to be important, and the text of each annual report will give all the refinements of data which may be needed in theoretical discussions. Only such changes in the table as seem to be absolutely necessary need be made during the next two years, and that they should seriously affect the values in common use is highly improbable.

Since the annual report for 1913 was prepared, a number of important memoirs on atomic weights have appeared, which may be summarised as follows:

Nitrogen.—Scheuer (*Anzeiger Wien Akad.*, 1912, **49**, 36), from analyses of nitrogen trioxide and tetroxide, and from measurements of ratios connecting the oxides of nitrogen, finds $N = 14.008$ as the mean of five series of determinations. He also determined the densities of ammonia and of sulphur dioxide, obtaining results in accordance with earlier investigations. The value assigned to N varies from the rounded-off figure given in the table by only one part in 7000.

Chlorine.—By the synthesis of NOCl , by the direct union of nitric oxide and chloride, Wourtsel (*Compt. rend.*, 1912, **155**, 345) finds $\text{Cl} = 35.4596$, when $N = 14.008$. He also (*Compt. rend.*, 1912, **155**, 152) determined the density of nitrosyl chloride, and found the weight of the normal litre to be 2.9919 grams. From this he

deduced a molecular weight of 65.456, which is probably too low. From the ratio between ammonia and hydrochloric acid, re-measured by Baume and Perrot (*Compt. rend.*, 1912, **155**, 461), the authors found $\text{Cl}=35.463$, an unusually high value. None of these new determinations warrants any change in the accepted figure for chlorine.

Bromine.—By the direct synthesis of hydrobromic acid from weighed quantities of hydrogen and bromine, Weber (*J. Amer. Chem. Soc.*, 1912, **34**, 1294) finds $\text{Br}=79.3066$ when $\text{H}=1$. With $\text{O}=16$, the value for bromine becomes 79.924. The accepted value differs from this by only 1 part in 20,000.

Phosphorus.—Baxter and Moore (*J. Amer. Chem. Soc.*, 1912, **34**, 1644), from analyses of phosphorus trichloride, find $\text{P}=31.018$, in good agreement with previous determinations. This is slightly lower than the value given in the table.

Iron.—By the reduction of ferric oxide in hydrogen, Baxter and Hoover (*J. Amer. Chem. Soc.*, 1912, **34**, 1657) find $\text{Fe}=55.847$.

Cadmium.—The electrochemical equivalent of cadmium has been determined by Laird and Hulett (*Trans. Amer. Electrochem. Soc.*, **22**, 385), who precipitated cadmium and silver simultaneously in an electric current. From the data given, the atomic weight of cadmium is 112.31, a low value, but one in accord with the previous work of Hulett and Perdue on cadmium sulphate. The investigation is to be continued with the chloride.

Tellurium.—The supposed complexity of tellurium has been re-investigated by Dudley and Bowers (*J. Amer. Chem. Soc.*, 1913, **35**, 875), with negative results. They attempted to determine the atomic weight by the basic nitrate method, which they found to be unsatisfactory. A series of syntheses of the tetrabromide gave $\text{Te}=127.479$.

Uranium.—From calcinations of uranyl nitrate to uranium dioxide, Lebeau (*Compt. rend.*, 1912, **155**, 161) found $\text{U}=238.54$. Echsner de Coninck (*Compt. rend.*, 1912, **155**, 1511), by calcination of uranic oxalate, obtained variable results, in mean, $\text{U}=238.44$.

Scandium.—Atomic weight redetermined by Meyer and Goldenberg (*Chem. News*, 1913, **106**, 12), who employed the sulphate method. In mean, $\text{Sc}=44.14$, in agreement with the accepted value. The higher figure given by Meyer and Winter was due to the presence of thoria in the material employed.

Yttrium.—Two determinations of the atomic weight by Meyer and Wuorinen (*Zeitsch. anorg. Chem.*, 1913, **80**, 7) gave $\text{Yt}=88.6$. The sulphate method was used. Egan and Balke (*J. Amer. Chem. Soc.*, 1913, **35**, 365), in a preliminary study of the ratio between yttrium chloride and yttria, found $\text{Yt}=90.12$. As their research is

to be continued, it would be unwise to use either of these investigations as a basis for changing the table. The lower of the two values appears to be the more probable.

Ruthenium.—Vogt (*Sitzungsber. phys. med. Soz. Erlangen*, **43**, 268), from reductions of ruthenium dioxide, finds $Ru=101.63$.

Palladium.—Determinations of atomic weight by analysis of palladiumammonium chloride have been made by Shinn (*J. Amer. Chem. Soc.*, 1912, **34**, 1448). The mean value obtained was $Pd=106.709$, but the individual determination varied more than is satisfactory. Shinn supposes that the chloride is less definite than it has been assumed to be.

Radium.—From analyses of radium bromide, Hönigschmid (*Monatsh.*, 1913, **34**, 283) finds $Ra=225.97$, in confirmation of his former analysis of the chloride. The discordance between this value and the higher value obtained by others is unexplained. The presumption is in favour of Hönigschmid's determination, but a change in the table may well be deferred until more evidence is available.

The following table is that of 1913, unchanged.

(Signed) F. W. CLARKE.
W. OSTWALD.
T. E. THORPE.
G. URBAIN.

1914.

International Atomic Weights.

O = 16.			O = 16.		
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	144·3
Argon	A	39·88	Neon	Ne	20·2
Arsenic	As	74·96	Nickel	Ni	58·68
Barium	Ba	137·37	Niton (radium emanation)	Nt	222·4
Bismuth	Bi	208·0	Nitrogen	N	14·01
Boron	B	11·0	Osmium	Os	190·9
Bromine	Br	79·92	Oxygen	O	16·00
Cadmium	Cd	112·40	Palladium	Pd	106·7
Cæsium	Cs	132·81	Phosphorus	P	31·04
Calcium	Ca	40·07	Platinum	Pt	195·2
Carbon	C	12·00	Potassium	K	39·10
Cerium	Ce	140·25	Praseodymium	Pr	140·6
Chlorine	Cl	35·46	Radium	Ra	226·4
Chromium	Cr	52·0	Rhodium	Rh	102·9
Cobalt	Co	58·97	Rubidium	Rb	85·45
Columbium	Cb	93·5	Ruthenium	Ru	101·7
Copper	Cu	63·57	Samarium	Sa	150·4
Dysprosium	Dy	162·5	Scandium	Sc	44·1
Erbium	Er	167·7	Selenium	Se	79·2
Europium	Eu	152·0	Silicon	Si	28·3
Fluorine	F	19·0	Silver	Ag	107·88
Gadolinium	Gd	157·3	Sodium	Na	23·00
Gallium	Ga	69·9	Strontium	Sr	87·63
Germanium	Ge	72·5	Sulphur	S	32·07
Glucinum	Gl	9·1	Tantalum	Ta	181·5
Gold	Au	197·2	Tellurium	Te	127·5
Helium	He	3·99	Terbium	Tb	159·2
Holmium	Ho	163·5	Thallium	Tl	204·0
Hydrogen	H	1·008	Thorium	Th	232·4
Indium	In	114·8	Thulium	Tm	168·5
Iodine	I	126·92	Tin	Sn	119·0
Iridium	Ir	193·1	Titanium	Ti	48·1
Iron	Fe	55·84	Tungsten	W	184·0
Krypton	Kr	82·92	Uranium	U	238·5
Lanthanum	La	139·0	Vanadium	V	51·0
Lead	Pb	207·10	Xenon	Xe	130·2
Lithium	Li	6·94	Ytterbium (Neoytterbium)	Yb	172·0
Lutecium	Lu	174·0	Yttrium	Yt	89·0
Magnesium	Mg	24·32	Zinc	Zn	65·37
Manganese	Mn	54·93	Zirconium	Zr	90·6
Mercury	Hg	200·6			

CLXXXVII.—*The Neutral and Acid Oxalates of Potassium.*

By HAROLD HARTLEY, JULIEN DRUGMAN, CHARLES ARCHIBALD VLIeland, and ROBERT BOURDILLON.

THE equilibrium in the system potassium hydroxide-oxalic acid-water has already been studied by Koppel and Cahn (*Zeitsch. anorg. Chem.*, 1908, **60**, 53) at various temperatures, and by Foote and Andrew at 25° (*Amer. Chem. J.*, 1905, **34**, 153). A fresh study has been made of the equilibrium at 25°, and two doubtful points have been investigated, namely, an anomaly in the solubility of the neutral potassium oxalate stated by Koppel to exist in the neighbourhood of 10°, and the degree of hydration and transition temperature of the hydrated potassium hydrogen oxalate. Further, the tetrapotassium dihydrogen oxalate first observed by Koppel and Cahn, and a new twinned form of the neutral oxalate, have been examined crystallographically by Dr. Drugman.

Equilibrium at 25°.

Solubility measurements at 25° were made with solutions containing the acid and base in proportions varying between $K_2C_2O_4$ and $H_2C_2O_4$; these were stirred in a thermostat regulated to 0.02° for some days; weighed quantities were then withdrawn, and analysed by titration against permanganate and baryta. With the exception of Nos. 10 and 13, each value is the mean of at least

No.	Grams of K_2O per 100 grams of solution.	Grams of C_2O_3 per 100 grams of solution.	Equiv. conc. of acid Equiv. conc. of acid + equiv. conc. of base.	Solid phase in equilibrium with solution.
1	0.0	8.290	1.0	$H_2C_2O_4 \cdot 2H_2O$
2	0.045	8.278	0.996	$H_2C_2O_4 \cdot 2H_2O +$ $KH_3(C_2O_4)_2 \cdot 2H_2O$
3	0.064	7.412	0.994	$KH_3(C_2O_4)_2 \cdot 2H_2O$
4	0.238	2.827	0.940	$KH_3(C_2O_4)_2 \cdot 2H_2O$
5	0.246	2.445	0.929	$KH_3(C_2O_4)_2 \cdot 2H_2O$
6	0.346	2.007	0.884	$KH_3(C_2O_4)_2 \cdot 2H_2O$
7	0.555	1.790	0.808	$KH_3(C_2O_4)_2 \cdot 2H_2O$
8	0.567	1.734	0.800	$KH_3(C_2O_4)_2 \cdot 2H_2O$
9	1.714	2.675	0.671	$KH_3(C_2O_4)_2 \cdot 2H_2O$
10	2.052	3.079	0.663	$KH_3(C_2O_4)_2 \cdot 2H_2O$
11	2.360	3.450	0.657	$KH_3(C_2O_4)_2 \cdot 2H_2O +$ KHC_2O_4
12	3.199	3.793	0.608	KHC_2O_4
13	5.919	5.457	0.547	KHC_2O_4
14	11.96	9.816	0.518	$KHC_2O_4 +$ $2K_2C_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$
15	15.71	12.365	0.507	$2K_2C_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O +$ $K_2C_2O_4 \cdot H_2O$
16	15.51	11.85	0.500	$K_2C_2O_4 \cdot H_2O$

two analyses; both permanganate and baryta were standardised against solutions of Kahlbaum's purest potassium quadroxalate. The results obtained are tabulated on p. 1747.

No. 14 is taken from Foote and Andrew's table, but is included above, as it is a triple point which was not determined by the authors. The values agree fairly well with those of Foote and Andrew, except Nos. 4 and 5, which differ greatly from the values obtained by drawing a curve through Foote and Andrew's points. As they were made at different dates by independent observers, and the solutions had been stirred for some days before analysis, we are inclined to trust them. The value found for pure oxalic acid is 1.5 per cent. higher than that found by Foote and Andrew. After trying various methods of graphical representation, we decided to plot the concentration of acid anhydride against the quantity $\frac{\text{equiv. conc. of acid}}{\text{equiv. conc. of acid} + \text{equiv. conc. of base}}$, as in this way the relation of the composition of the solid phase to that of the solution is at once obvious.

Neutral Potassium Oxalate, $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

The solubility of this salt in neutral solution was measured at a number of temperatures with the following results:

Temperature.	Grams of $\text{K}_2\text{C}_2\text{O}_4$ per 100 grams of solution.
0.02°	20.33
5.05	21.78
9.84	23.08
20.05	25.85
25.15	27.37
29.98	28.36

These values agree with Koppel and Cahn's results at 0° and 30°, but are considerably lower at intermediate temperatures; when plotted, they give a smooth solubility curve. Each value is the mean of at least two analyses made after prolonged stirring in a thermostat kept within 0.03° of the stated temperature.

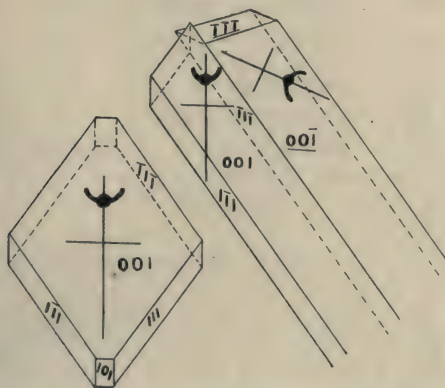
Some preliminary experiments were made in the hope of discovering a new hydrate, the existence of which had been suggested by Koppel and Cahn's anomalous solubility curve. No such hydrate was found.

Crystallisation from acid solution seems to favour the twinning of the neutral oxalate. It is only when the solution becomes nearly neutral that the ordinary untwinned crystals appear at all. The ordinary habitus of this salt, which crystallises in the monoclinic system, is that of tabular plates of rhombic outline with bevelled edges, showing the following combination: (001) (111) (11 $\bar{1}$)

predominant, and (100) (011) ($10\bar{1}$) subordinate. The flattening is parallel to the (001) face. The twinned crystals are, on the contrary, of long-prismatic habitus, also flattened parallel to (001). The relation between the two parts of the twin is expressible by a rotation of 180° about the edge (001)/(111), and (111) is composition-plane. The basal faces of the two crystals lie in the same plane, but their line of junction, which runs parallel to the length of the crystal, is very plainly noticeable on it. Under crossed nicols the overlapping strip remains light in all positions.

The presence of this somewhat unusual mode of twinning is clearly indicated by the direction of emergence of the one optic axis visible on the basal plane, as shown in the diagram (Fig. 1). The extinction is symmetric to the median line, but the optic axis

FIG. 1.



Simple and twin crystals of neutral potassium oxalate.

emerges unsymmetrically in the two halves. The face ($10\bar{1}$) is generally developed at the end of the twinned crystal, thus almost obliterating any re-entrant angle, but this has been left out in the figure, for greater clearness, and only the most elementary faces are shown.

The twinned crystals on analysis gave results agreeing closely with the formula $K_2C_2O_4 \cdot H_2O$.

Potassium Hydrogen Oxalate, $2KHC_2O_4 \cdot H_2O$.

It was found (as inferred from Koppel and Cahn's curves) that potassium hydrogen oxalate was easily made by cooling hot solutions containing about 22 grams of K_2O and 24 grams of C_2O_3 per 100 grams of water. Above 15° only the anhydrous salt was deposited.

At temperatures below 10° a mixture of the anhydrous salt and hemihydrate was always obtained. The mixture could be converted to either pure salt by stirring for a day or two in a bottle kept below 5° or above 10° respectively. It was easy to test the purity of both forms, as the hemihedral plates of the hydrated salt are easily distinguished with a microscope from the rhombic prisms of the anhydrous compound. The hydrated crystals thus obtained were washed quickly by the aid of the pump, and, owing to their rapid efflorescence, dried as rapidly as possible between numerous changes of filter paper, and weighed at once. They were analysed by titration against permanganate and baryta, and the following results were obtained:

	Found.			Calc.	Calc.
	A.	B.	C.	$2\text{KHC}_2\text{O}_4, \text{H}_2\text{O}$.	$\text{KHC}_2\text{O}_4, \text{H}_2\text{O}$.
K_2O per cent. ...	34.83	34.17	34.16	34.36	32.24
C_2O_3 „ ...	53.15	52.29	52.38	52.52	49.28
H_2O „ by difference	12.02	13.54	13.46	13.13	18.48

Analyses B and C were made in winter, but A was made in summer, when some efflorescence seems to have occurred during drying. The formula thus appears to be $2\text{KHC}_2\text{O}_4, \text{H}_2\text{O}$, as found by the earlier observers, Rammelsberg and Marignac, and not $\text{KHC}_2\text{O}_4, \text{H}_2\text{O}$, as stated by Wyruboff.

Transition Temperature, $2\text{KHC}_2\text{O}_4, \text{H}_2\text{O} \rightleftharpoons \text{KHC}_2\text{O}_4$.

Preliminary experiments with a dilatometer having proved unsuccessful, the transition temperature was determined approximately by stirring a mixture of crystals of the two compounds in a saturated solution in a thermostat, and observing the resulting changes by microscopic examination. It was thus found that at temperatures above 7.4° , the anhydrous crystals grew at the expense of the hydrated, whilst at temperatures below 5.4° , the reverse change occurred. At 6° and 6.8° , the change was too slow to be noticeable, even after sixty hours' stirring. Hence the transition point lies near 6.4° .

Tetrapotassium Dihydrogen Oxalate, $2\text{K}_2\text{C}_2\text{O}_4, \text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$.

This salt was prepared from solutions of the concentration suggested by Koppel and Cahn's solubility curves; its composition was found to agree with that given by those authors:

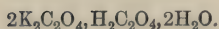
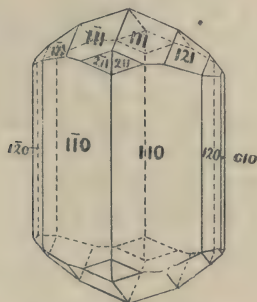
	Found.	Calc. for $2\text{K}_2\text{C}_2\text{O}_4, \text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$.
C_2O_3 per cent.	47.02	47.16
K_2O „	41.07	41.05
H_2O „	11.91	11.79

Crystallographic measurements gave the following results:

System orthorhombic: $a:b:c=0.5370:1:0.3555$.

Forms observed: (110) (120) (111) (121) (131) (010) (211), nearly always fully developed. (100) (231) are rarer and (112) (140) have only been observed in one crystal, and there only in alternate octants. (The latter fact seems to point to the presence of less than the full symmetry of the orthorhombic system, but no confirmation, by etch-figures, has so far been obtained.) The habit is prismatic, with elongation parallel to the c -axis (Fig. 2). The

FIG. 2.



crystals generally grow on a face of {110}, and are then symmetrically developed; but sometimes they lie on (010) and then this face and the two prism faces ($\bar{1}\bar{1}0$) and ($\bar{1}\bar{1}0$) above become predominant, and the prism shows a triangular section.

The presence of vicinal faces and striation is accountable for some wide variations between the calculated and observed values.

	Observed.	Calculated.		Observed.	Calculated.
110— $\bar{1}\bar{1}0$	56°28'	—	010—140	25° 4'	24°58'
110—111	53 4	—	120—140	17½°	18°
110—120	18 40	18°48'5'		(approx.)	
111— $\bar{1}\bar{1}1$	63 53	63 56	No cleavage could be detected. The extinction is parallel to the prism zone. (010) is the plane of the optic axis, and the axial angle is fairly large, so that no axial image is visible in convergent light on any of the faces occurring. Axis c is the acute bisectrix and $n_\gamma \parallel$ axis a , that is, the crystal is negative biaxial. The refractive indices, determined with the total-reflectometer for sodium light are, approximately, $n_\gamma=1.55$, $n_\beta=1.52$, $n_\alpha=1.48$, and $n_\gamma-n_\alpha=0.03$.		
111— $\bar{1}\bar{1}1$	33 14	33 2			
111—120	—	55 20			
111—121	14 7	14 9			
111—211	19 22	19 20			
121— $\bar{1}\bar{2}1$	56 25	56 43			
121—120	46 4	45 48			
121—131	10 46	10 59			
131—010	48 30	48 21			
131—120	40 25	39 52			
131— $\bar{1}\bar{3}1$	48 45	48 44			
010—231	77 55	77 55			
231—131	17 33	17 48			

CLXXXVIII.—*The Chemistry of the Glutaconic Acids.*
Part X. The Alkylation of the Ethereal Salts.

By JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD.

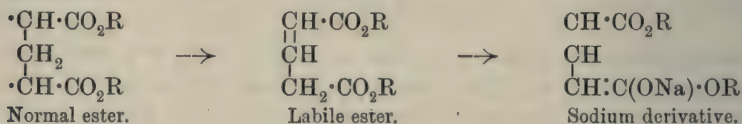
DURING the course of the experiments described in the preceding parts of this series evidence has accumulated which shows the mechanism by which esters of the glutaconic acids can be transformed into their alkyl derivatives, and from this evidence the following generalisations can be derived:

(1) *The formation of the sodium derivative of an ester of a glutaconic acid, and hence the formation of an alkyl derivative, takes place through the labile form of the ester alone.*

(2) *The normal esters, as such, do not react with sodium ethoxide.*

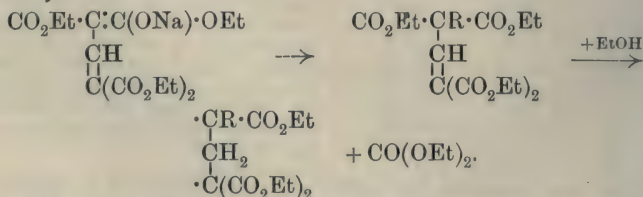
(3) *The formation of a sodium derivative of a normal ester is therefore dependent on the tendency for the ester to pass into the labile modification under the experimental conditions employed.*

These generalisations may be expressed by the following formulæ:



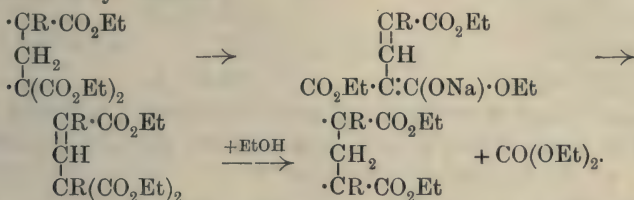
For the purpose of showing that the different types of ester conform to these generalisations, it is advisable to divide them into three classes:

(a) *The Tetracarboxylic Esters.*—The only ester of this kind is ethyl dicarbethoxyglutaconate. The well-known yellow sodium derivative of this ester yields the *C*-alkyl derivative with alkyl iodides. In this alkyl derivative the "labile" structure must necessarily be fixed; it therefore reacts with alcoholic sodium ethoxide, yielding ethyl carbonate and the normal ester of the tricarboxylic acid:



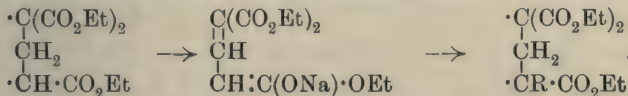
(b) *The Tricarboxylic Esters.*—The formation of a sodium derivative from an ester of this type, formed as shown above, involves

the replacement of the mobile hydrogen atom; the sodium atom therefore takes up the most negative position in the system (compare T., 1912, **101**, 250), and yields the corresponding alkyl derivative with alkyl iodides:

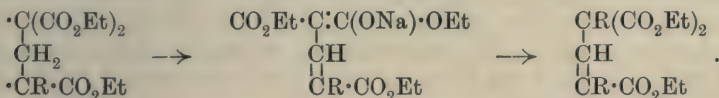


In this alkylated ester the "labile" structure is also fixed, and it therefore reacts with sodium ethoxide, yielding the dicarboxylic ester and ethyl carbonate.

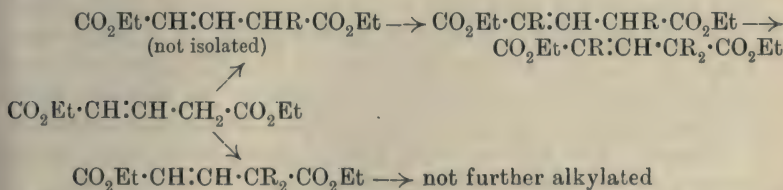
On the other hand, the alkylation of an unsubstituted tricarboxylic ester leads to the replacement of the hydrogen atom at the other end of the chain, the compound forming a sodium derivative, which retains the mobile hydrogen atom (*loc. cit.*, p. 252):



This compound then reacts with sodium ethoxide, without the elimination of ethyl carbonate, and from this the dialkyl derivative can be formed:

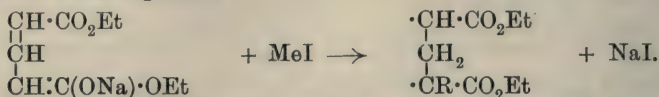


The Dicarboxylic Esters.—The systematic alkylation of ethyl glutaconate, the simplest member of this series, has been investigated by Blaise (*Compt. rend.*, 1903, **136**, 381, 692, 1140; *Bull. Soc. chim.*, 1903, [iii], **29**, 1015), whose results may be shown as follows:

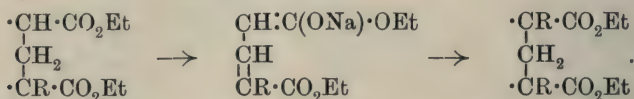


The formation of the α -dimethyl derivative in this manner is certainly remarkable, especially when it is remembered that, in the original preparation of this substance, Henrich (*Monatsh.*, 1899, **20**, 539) used equimolecular quantities of the ester, sodium ethoxide, and methyl iodide,

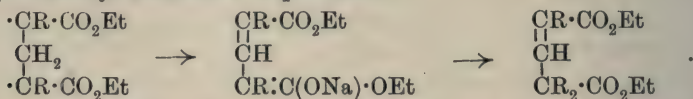
Our own experiments show that when the pure sodium derivative of ethyl glutaconate is treated with methyl iodide in dry ethereal solution, its conversion into the monomethyl derivative in accordance with the equation



is complete, and that when the ester of α -methylglutaconic acid, formed in this manner, is again alkylated the product is composed entirely of the $\alpha\gamma$ -dialkyl derivative:



When this normal ester is again treated with sodium ethoxide and an alkyl iodide, the mobile hydrogen atom is displaced and the $\alpha\alpha\gamma$ -trimethyl derivative is produced:

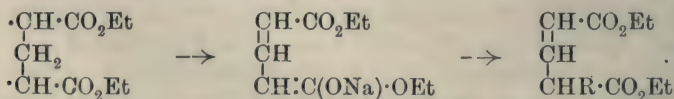


It follows, therefore, that the behaviour of these compounds can be expressed by the generalisation:

(4) *The formation of a sodium derivative from a normal ester of a mono-alkylated dicarboxylic acid involves the passage of the mobile hydrogen atom to the carbonyl system not affected by the substituting group. The second alkyl group therefore enters on the carbon atom of the three-carbon system most remote from that bearing the existing alkyl group.*

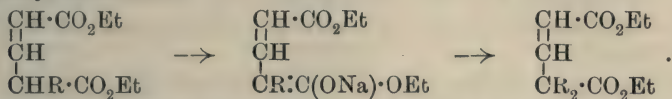
The formation of ethyl $\alpha\alpha$ -dimethylglutaconate in the manner described by Henrich and by Blaise must be regarded as an abnormal reaction, for which, however, an explanation is readily forthcoming.

Our experiments show that the transformation of ethyl glutaconate into its sodium derivative by the action of an equivalent amount of sodium ethoxide in alcohol is far from complete, and that nearly half the ester remains unaltered in solution, there being, of course, an equivalent quantity of free sodium ethoxide also present. The first action of methyl iodide leads, then, to the formation of the labile methyl ester:

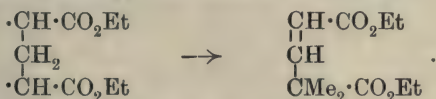


but the presence of sodium ethoxide prevents this labile ester from

passing into its normal form, and it is therefore again transformed into a sodium derivative, from which methyl iodide forms the dimethyl derivative:



The truth of this explanation is shown by the fact that when ethyl glutaconate is methylated in the presence of more than twice the equivalent amount of sodium ethoxide, its transformation into the $\alpha\alpha$ -dimethyl derivative is complete:

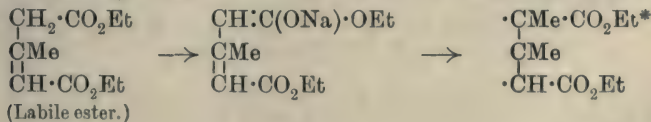


This further generalisation is therefore necessary:

(5) *Those esters which contain two or three potentially mobile hydrogen atoms can be made to yield dialkyl derivatives having the alkyl groups on the same carbon atom by alkylating them under conditions which prevent the passage of the labile alkyl derivative, which is first formed, into its normal isomeride. This can be effected by the presence of excess of sodium ethoxide throughout the alkylation.*

The normal esters of the alkylglutaconic acids mentioned above, which have the alkyl groups on the terminal atoms of the three-carbon system, have the movable hydrogen atom in so mobile a condition that it is probably impossible to isolate the corresponding labile esters in a pure condition, and no evidence can therefore be derived from them respecting the behaviour of the two forms on alkylation. It is only by the entrance of an alkyl group on the central carbon atom of the system that sufficient stability is conferred on the two modifications to enable them to supply definite evidence on this point.

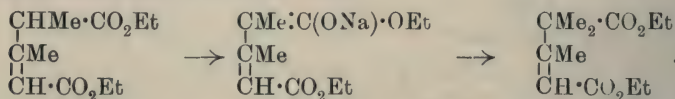
It has already been shown (T., 1912, 101, 1557) that it is an easy matter to prepare both the normal and labile esters of β -methylglutaconic acid in a pure condition, and experiment proves that, whereas the labile ester is completely converted into the dimethyl derivative by alcoholic sodium ethoxide and methyl iodide at the ordinary temperature, the normal ester, under the same



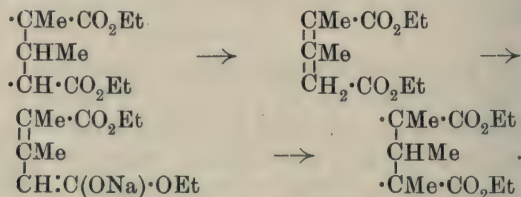
* The product formed in this reaction is a mixture of the normal and labile esters.

experimental conditions, is quite unchanged. The normal ester can, however, be alkylated in a sealed tube at 120°, as shown by Feist and Beyer (*Annalen*, 1906, **345**, 123), because, under these conditions, the ester is converted into the sodium derivative of the labile form.

The formation of the sodium derivative from the labile ester is evidently complete under these conditions, because, unlike ethyl glutaconate in similar circumstances, no formation of the $\alpha\alpha\beta$ -trimethyl derivative was noticed. The labile ester may, nevertheless, be made to conform to the generalisation (5) by alkylating it in the presence of excess of sodium ethoxide when ethyl $\alpha\alpha\beta$ -trimethylglutaconate is formed, thus:



The further alkylation of normal ethyl $\alpha\beta$ -dimethylglutaconate (prepared from the normal acid) requires a high temperature, and then yields the $\alpha\beta\gamma$ -trimethyl derivative. The methylation of the labile ester (T., 1912, **101**, 1567) can, however, be effected at the ordinary temperature:



The production of the tetramethyl derivative from the trimethyl ester could not be effected.

It should also be mentioned that in certain cases even the labile form of a substituted ester may fail to yield a sodium derivative. This only happens when the entrance of substituting groups on the carbon atoms of the three-carbon system completely inhibits the movement of the hydrogen atom. The only case of this kind which has yet come under our notice is that of ethyl α -carbethoxy- β -phenyl- α -methylglutaconate (this vol., p. 1574), which can be isolated in the two forms:



neither of which reacts with alcoholic sodium ethoxide.

The final generalisation is therefore as follows:

(6) *Esters, although they may have the labile structure, will not*

react with sodium ethoxide if the nature of the groups carried by the carbon atoms of the three-carbon system is such as to prevent the movement of the hydrogen atom within the molecule.

EXPERIMENTAL.

The Sodium Derivative of Ethyl Glutaconate.

We find that this substance can be prepared in a condition sufficiently pure for analysis by adding dry ether to the solution obtained by mixing the ester with an equivalent amount of sodium ethoxide dissolved in alcohol. The yellow, crystalline precipitate is further purified by washing with dry ether. (Found, Na=10.91. $C_9H_{13}O_4Na$ requires Na=11.06 per cent.)

During this preparation it was evident that the conversion of the ester into its sodium derivative is only partial; for example, when 18.6 grams of ethyl glutaconate are added to a solution of 2.3 grams of sodium dissolved in 25 grams of alcohol and the yellow sodium derivative is completely precipitated by dry ether, 8.7 grams of unaltered ester can be recovered from the filtrate.

The Methylation of the Sodium Derivative.

The transformation of the yellow sodium compound into ethyl α -methyl glutaconate can be effected by suspending the pure salt in dry ether, adding the requisite amount of methyl iodide, and then shaking the well-cooled mixture until the yellow colour has disappeared. The product distils at $244^\circ/754$ mm. (Found, C=59.86; H=8.12. $C_{10}H_{16}O_4$ requires C=60.0; H=8.0 per cent.) The ester gave α -methylglutaconic acid, melting at 145 — 146° , on hydrolysis.

The Methylation of Ethyl α -Methylglutaconate.

The methylation was effected by means of an equivalent amount of sodium ethoxide and methyl iodide in alcohol at 12 — 14° . It was found, however, by an analysis of the product, that quite half of the monoalkyl ester remained unchanged under these conditions. The methylation was therefore repeated three times, steps having been taken in the first instance to show that the dimethyl derivative did not undergo further methylation under the experimental conditions employed. *Ethyl $\alpha\gamma$ -dimethylglutaconate*, $CO_2Et \cdot \dot{C}Me \cdot CH_2 \cdot \dot{C}Me \cdot CO_2Et$, is a mobile oil boiling at $179^\circ/80$ mm.:

0.1901 gave 0.4296 CO_2 and 0.1421 H_2O . C=61.63; H=8.31.

$C_{11}H_{18}O_4$ requires C=61.7; H=8.4 per cent.

This ester has been described in Part I. of this series (T., 1911, 99, 2203), but it is evident from the analysis given there that the compound is the methyl ethyl ester, and that the name "*Methyl Ethyl α -Dimethylglutaconate*" should be placed at the head of the paragraph.

It is probable that the ester prepared above is pure, and does not contain any appreciable amount of the methyl ethyl ester of the trimethylated acid. α -Dimethylglutaconic acid melting at 147° was the only substance which could be isolated from it on hydrolysis.

The Methylation of Ethyl Glutaconate in the Presence of Excess of Sodium Ethoxide.

In carrying out this experiment, 18.6 grams of ethyl glutaconate were added to a solution containing 5.6 grams of sodium dissolved in 65 grams of alcohol, and after excess of methyl iodide had been added the whole was shaken under running water until all colour had disappeared. The product boiled at $163^{\circ}/50$ mm. (Found, C=61.59; H=8.45. $C_{11}H_{18}O_4$ requires C=61.7; H=8.4 per cent.) The ester on hydrolysis yielded a mixture of acids, from which *cis*- α -dimethylglutaconic acid melting at 135° was readily isolated. From the residues a small quantity of the *trans*-acid melting at 172° was isolated by the aid of acetyl chloride, but no other acid could be separated.

The Methylation of Normal and Labile Ethyl β -Methylglutaconate.

(1) *With an Equivalent Amount of Sodium Ethoxide.*—Twenty grams of the labile ester were added to an alcoholic solution containing 2.3 grams of sodium, and, after excess of methyl iodide had been added, the mixture was shaken under running water until all colour had disappeared. Ethyl $\alpha\beta$ -dimethylglutaconate, $CO_2Et \cdot CMe \cdot CMe \cdot CH \cdot CO_2Et$,* which was isolated in the usual manner, is a mobile liquid melting at $176^{\circ}/76$ mm. (Found, C=61.67; H=8.39. $C_{11}H_{18}O_4$ requires C=61.7; H=8.4 per cent.)

The ester yields $\alpha\beta$ -dimethylglutaconic acid, melting at 148° , on hydrolysis.

The normal ester when treated in the same manner is recovered unchanged, although methylation is effected in a sealed tube at 120° in the manner described by Feist and Beyer (*loc. cit.*).

(2) *With Excess of Sodium Ethoxide.*—In this experiment the same amount of labile ester was used, but it was mixed with an

* See footnote, p. 1755.

alcoholic solution of 5.6 grams of sodium and an equivalent quantity of methyl iodide was added. The heat of the reaction was controlled by running water, the product being isolated as soon as all colour had disappeared. *cis*-Ethyl $\alpha\beta$ -trimethylglutaconate, $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, is a mobile liquid boiling at $164^\circ/45$ mm.:

0.1765 gave 0.4081 CO_2 and 0.1407 H_2O . $\text{C}=63.07$; $\text{H}=8.86$.

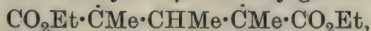
$\text{C}_{12}\text{H}_{20}\text{O}_4$ requires $\text{C}=63.2$; $\text{H}=8.8$ per cent.

When the ester is hydrolysed by dilute hydrochloric acid the anhydride of *cis*- $\alpha\beta$ -trimethylglutaconic acid melting at 107° separates when the clear solution is cooled (Found, $\text{C}=62.21$; $\text{H}=6.59$. $\text{C}_8\text{H}_{10}\text{O}_3$ requires $\text{C}=62.3$; $\text{H}=6.5$ per cent.) (compare Perkin and Thorpe, T., 1897, **71**, 1184).

The anhydride was identified by conversion into the acid melting at 133° by the action of cold dilute alkali. No trace of the *trans*-acid melting at 148° could be found accompanying this compound, and this fact is in complete accordance with our view that both the normal and labile modifications of the acids of this series have the *cis*-configuration (T., 1912, **101**, 1740). It is therefore certain that the above ester is the *cis*-modification, and that the ester previously prepared (T., 1897, **71**, 1183) is the *trans*-isomeride.

The Methylation of the Normal and Labile Esters of Ethyl $\alpha\beta$ -Dimethylglutaconate.

The manner in which these esters can be prepared has been described (T., 1912, **101**, 1567). When the labile ester (21.4 grams) is added to a solution containing 2.3 grams of sodium in alcohol and is mixed with excess of methyl iodide, the methylation is complete at the end of three hours at the temperature of running water. The product is ethyl $\alpha\beta\gamma$ -trimethylglutaconate,



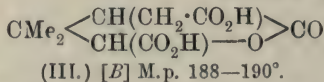
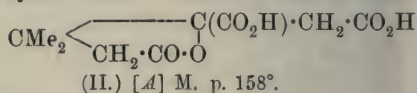
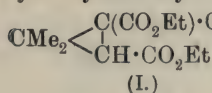
a mobile oil boiling at $164^\circ/50$ mm. (Found, $\text{C}=63.13$; $\text{H}=8.91$. $\text{C}_{12}\text{H}_{20}\text{O}_4$ requires $\text{C}=63.2$; $\text{H}=8.8$ per cent.) (compare T., 1905, **87**, 1707). The ester is converted into $\alpha\beta\gamma$ -trimethylglutaconic acid, melting at 127° , on hydrolysis.

The normal ester remains unaltered after treatment in the same manner, but is converted into the trimethyl derivative when the mixture as above is heated in a sealed tube at 120° for five hours.

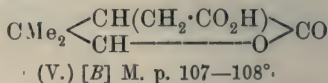
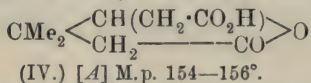
CLXXXIX.—*Note on the Structure of Certain Lactones Formed by the Fission of the gem.-Dimethylcyclopropane Ring.*

By WILLIAM HENRY PERKIN, jun., and JOCELYN FIELD THORPE.

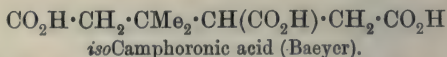
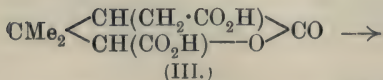
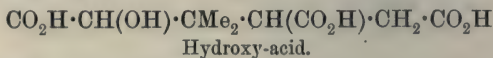
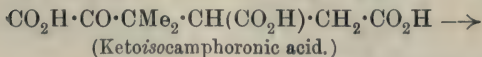
DURING the course of our experiments on the synthetical formation of bridged rings (T., 1901, **79**, 764) we subjected ethyl dicarboethoxydimethylcyclopropanemalonate (I) to the action of alcoholic potassium hydroxide, and isolated two lactone-dicarboxylic acids (II and III), which we named the lactones of the *A* and *B* hydroxydimethylbutanetricarboxylic acids. These lactones were



characterised by the fact that, when heated at 190°, carbon dioxide was eliminated and two lactone-monocarboxylic acids, which we named the lactones of the *A* and *B* hydroxydimethylbutanedicarboxylic acids (IV and V), were produced:

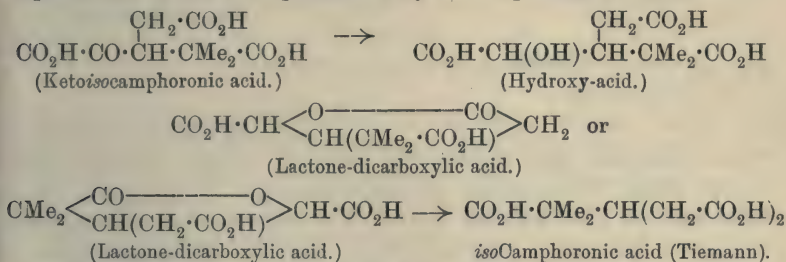


We were unable, at that time, to distinguish between the *A* and *B* forms of these lactones, and, moreover, we did not notice that the formula III had been assigned by Baeyer (*Ber.*, 1896, **29**, 2792) to a lactone-dicarboxylic acid which he had prepared by the reduction of ketoisocamphoronic acid with sodium amalgam, and which he had transformed into isocamphoronic acid by further reduction with hydriodic acid. These changes were represented by Baeyer in the following manner:



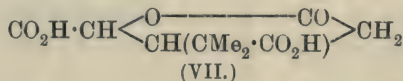
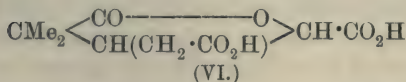
Baeyer's lactone-dicarboxylic acid is, however, quite different

from our *B* lactone-dicarboxylic acid, and, indeed, it is evident, in view of the establishment of the Tiemann formula for *isocamphoronic* acid by direct synthesis (Perkin and Thorpe, T., 1899, 75, 897; Perkin, *ibid.*, 1902, 81, 246), that the course of Baeyer's experiments must be represented by the expressions:

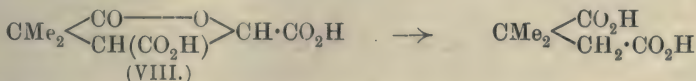


It is therefore curious that Aschan, in a recent paper (*Annalen*, 1913, 398, 299), should have reverted to the Baeyer formula of *isocamphoronic* acid, and should have assigned the formula III to a lactone-dicarboxylic acid which he has isolated in *cis*- and *trans*-forms, the *cis*-modification being evidently identical with the compound prepared by Baeyer.

Since the compounds prepared by Aschan both yield *isocamphoronic* acid on reduction with hydriodic acid, it follows that they must be the *cis*- and *trans*-forms of either lactone (VI) or (VII):



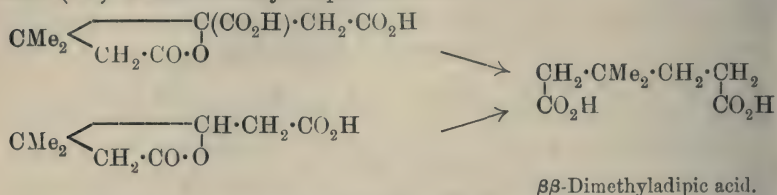
From the fact that Aschan's lactones yield formic, succinic, and *isobutyric* acids on fusion with potassium hydroxide, they must be the *cis*- and *trans*-forms of formula VII, because it is evident that a lactone of formula VI would yield, under these conditions, either *as*-dimethylsuccinic acid or, possibly, trimethylsuccinic acid in the same manner as the similarly constituted lactone (VIII) is transformed into *as*-dimethylsuccinic acid by fusion with potassium hydroxide (Baeyer, *loc. cit.*, 2795):



It therefore follows that the lactone-dicarboxylic acid prepared by Baeyer and by Aschan is not the same compound as the substance of formula III described by us.

We have, however, settled the question as to which of our

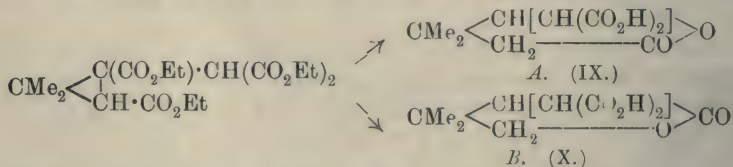
lactones has the *A* and which the *B* formula by reducing both the *A* lactone-dicarboxylic acid (II) and the *A* lactone-monocarboxylic acid (IV) to $\beta\beta$ -dimethyladipic acid:



The reduction was effected by treating either lactone with twenty times the quantity of hydriodic acid (b. p. 127°) in a sealed tube at 170° for four hours. The product was then evaporated until free from hydriodic acid, and the crystalline residue recrystallised from a mixture of chloroform and light petroleum. It melted at 86—87° (Found, C=55.09; H=8.07. $\text{C}_8\text{H}_{14}\text{O}_4$ requires C=55.2; H=8.0 per cent.). The acid was therefore $\beta\beta$ -dimethyladipic acid (compare Blanc, *Compt. rend.*, 1904, **139**, 800; Crossley and Renouf, T., 1906, **89**, 1552).

Unfortunately, the *B* lactones were found to undergo decomposition on being treated in the same manner, and no definite product could be isolated.

Although, however, the formation of $\beta\beta$ -dimethyladipic acid reveals the structure of the lactone-monocarboxylic acids IV and V, yet there are still alternative formulæ for the lactone-dicarboxylic acids II and III, because it is evident that the decomposition of ethyl dicarbethoxydimethylcyclopropanemalonate might yield the lactones IX and X, and, as a matter of fact, these

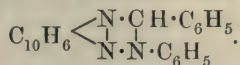


formulæ would account for the ready way in which these substances lose carbon dioxide. It is evident that these lactone-dicarboxylic acids would yield the lactone-monocarboxylic acids of formulæ IV and V when heated.

CXC.—*The Resolution of 2:3-Diphenyl-2:3-dihydro-1:3:4-naphthaisotriazine into Optically Active Components.*

By WILLIAM JACKSON POPE and CLARA MILLICENT TAYLOR.

THE constitution of the diphenyl- β -naphtha- α -dihydrotriazine first prepared by Goldschmidt and Rosell (*Ber.*, 1890, **23**, 487) may be regarded as satisfactorily established from the discussion by Meldola and Forster (*T.*, 1891, **59**, 679) as that of the 2:3-diphenyl-2:3-dihydro-1:3:4-naphthaisotriazine,



According to this constitutional formula the molecule contains an asymmetric carbon atom, and it would be therefore anticipated that the substance would exist in two optically active, enantiomorphously related isomerides. Further, Meldola and Forster (*loc. cit.*, p. 696) showed that the *p*-dinitro-derivative of this triazine, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \\ | \quad | \\ \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \end{array}$, is soluble in alkalis, and can be methylated by treatment with methyl iodide in the presence of sodium hydroxide and alcohol; it follows that the hydrogen atom attached to the asymmetric carbon atom is replaceable by sodium, and is hence labile. Since, in the formation of salts of the parent triazine, the nitrogen atom attached to the phenyl group presumably becomes quinquivalent, and this nitrogen atom is attached to the asymmetric carbon atom, it might be expected that the resolution of the triazine should be attended by autoracemisation. The particular type of autoracemisation which would be looked for has been observed in somewhat analogous cases by Pope and Harvey with *ac*-tetrahydro- β -naphthylamine (*T.*, 1901, **79**, 74), and by Pope and Clarke with 2-methyldihydroindole (*T.*, 1904, **85**, 1330); in explaining these cases it has been found necessary to presume the transient formation of an element of constitution containing the grouping, $\text{C} \cdot \text{NX}_3$, in which all the radicles attached to the nitrogen atom are basic in character. A similar supposition has been found necessary by Meldola and Hollely (*T.*, 1912, **101**, 912) in connexion with their work on the quinone-ammonium derivatives of picramic acid. It will be seen that the present paper furnishes another instance in which an explanation of the experimental results must be sought in the formation of an intermediate product containing the element of constitution referred to above.

2:3-Diphenyl-2:3-dihydro-1:3:4-naphthaisotriazine was prepared by the condensation of benzeneazo- β -naphthylamine with benzaldehyde under the conditions worked out by Meldola and Forster; after prolonged purification by crystallisation from alcohol and benzene it was obtained as a white, crystalline powder, melting at 198°, as found by Sachs and Goldmann (*Ber.*, 1902, **35**, 3351).

1-2:3-Diphenyl-2:3-dihydro-1:3:4-naphthaisotriazine
d- α -Bromocamphor- π -sulphonate.

An aqueous solution of a known weight of *d- α -bromocamphor- π -sulphonic acid*, prepared as described by Pope and Read (*T.*, 1910, **97**, 2199), was evaporated to a syrup and dissolved in an acetone solution of one molecular proportion of the triazine; after some time the salt of the triazine separates as a white, granular, crystalline powder. On fractionally crystallising the salt from acetone, evidence is obtained that it is a mixture, but, owing to the sparing solubility of the product in acetone, the fractional crystallisation is conveniently performed from solutions in methyl ethyl ketone, which boils at a higher temperature; after repeated crystallisation from this solvent a product of constant rotatory power is obtained. This substance forms a white, crystalline powder, which melts and decomposes at 220°:

0.1510 gave 0.3375 CO₂ and 0.0676 H₂O. C=60.9; H=5.0.

C₂₃H₁₇N₃, C₁₀H₁₅O₄BrS requires C=61.3; H=4.9 per cent.

The following determinations of rotatory power, like all the others quoted in the present paper, were made in 4-dcm. tubes at 20°, the weight of substance stated in grams being made up to 30 c.c. with the solvent:

Solvent: Alcohol. Wave- length.	0.0728 gram.		0.0702 gram.		Mean values.	
	α .	$[\alpha]$.	α .	$[\alpha]$.	$[\alpha]$.	$[M]$.
Hg, 5461	+0.36°	+37.1°	+0.34°	+36.3°	+36.7°	+237°
Hg, 5780	0.27	27.8	0.26	27.8	27.8	179
Na, 5893	0.25	25.7	0.24	25.6	25.7	166

Rotatory dispersions: Hg, 5461/Na, 5893=1.429; Hg, 5780/Na, 5893=1.082.

Solvent: Acetic acid.	0.1385 gram.		0.1612 gram.		Mean values.	
	α .	$[\alpha]$.	α .	$[\alpha]$.	$[\alpha]$.	$[M]$.
Hg, 5461	+0.64°	+34.6°	+0.73°	+33.9°	+34.3°	+222°
Hg, 5780	0.50	27.1	0.60	28.0	27.5	178
Na, 5893	0.44	23.8	0.51	23.8	23.8	154

Rotatory dispersions: Hg, 5461/Na, 5893=1.442; Hg, 5780/Na, 5893=1.156.

Solvent:	0.5080 gram.		0.5220 gram.		Mean values.	
Chloroform.						
Hg, 5461	-0.13°	-1.9°	-0.14°	-2.0°	-1.9°	-12.6°
Hg, 5780	0.11	1.6	0.11	1.5	1.6	10.1
Na, 5893	0.09	1.3	0.09	1.3	1.3	8.3

Rotatory dispersions: Hg, 5461/Na, 5893=1.518; Hg, 5780/Na, 5893=1.216.

d-2:3-Diphenyl-2:3-dihydro-1:3:4-naphthaisotriazine
d- α -Bromocamphor- π -sulphonate.

During the fractional crystallisation of the mixed salt from methyl ethyl ketone a quantity of the more soluble constituent of the mixture was accumulated; this presented external characters similar to those of the salt described above, and analysis showed it to have the same composition:

0.1426 gave 0.3182 CO₂ and 0.0633 H₂O. C=60.8; H=4.9.

C₂₃H₁₇N₃.C₁₀H₁₅O₄BrS requires C=61.3; H=4.9 per cent.

The following determinations of rotatory power show that this substance has a much higher dextro-rotation for the same wavelengths and solvents than the salt described above:

Solvent:	0.0772 gram.		0.0620 gram.		Mean values.	
Alcohol.						
Wave-length.	α .	$[\alpha]$.	α .	$[\alpha]$.	$[\alpha]$.	$[M]$.
Hg, 5461	+0.61°	+59.3°	+0.49°	+59.3°	+59.3°	+383
Hg, 5780	0.49	47.6	0.39	47.2	47.4	306
Na, 5893	0.45	43.7	0.36	43.6	43.6	282

Rotatory dispersions: Hg, 5461/Na, 5893=1.360; Hg, 5780/Na, 5893=1.087.

Solvent:	0.1692 gram.		0.1182 gram.		Mean values.	
Acetic acid.						
Hg, 5461	+1.20°	+53.2°	+0.84°	+53.3°	+53.2°	+344°
Hg, 5780	0.99	43.7	0.67	42.5	43.1	279
Na, 5893	0.83	36.8	0.58	36.8	36.8	238

Rotatory dispersions: Hg, 5461/Na, 5893=1.444; Hg, 5780/Na, 5893=1.172.

Solvent:	0.0804 gram.		0.1932 gram.		Mean values.	
Chloroform.						
Hg, 5461	+0.47°	+43.8°	+1.12°	+43.5°	+43.6°	+282°
Hg, 5780	0.40	37.3	0.95	36.9	37.1	239
Na, 5893	0.37	34.5	0.86	33.4	34.0	220

Rotatory dispersions: Hg, 5461/Na, 5893=1.282; Hg, 5780/Na, 5893=1.090.

The data which are quoted above prove that the salt formed from the triazine and the optically active acid is resolvable by crystallisation from methyl ethyl ketone into two well-characterised components; these can only represent the more or less pure salts, *lB,dA* and *dB,dA*. Since the salts are hydrolysed by water it is impossible to ascertain directly what part of the observed molecular rotations is due to the base and to the acid respectively. The

following unsuccessful attempts were made to separate an optically active base from the salts.

The base which remains insoluble on treating the salts *lB,dA* or *dB,dA* with sodium hydroxide solution is optically inactive in alcoholic solution; the base which slowly separates from the clear solution obtained by adding alcoholic potassium hydroxide solution to a suspension of either salt in alcohol is also optically inactive in alcoholic solution. The base, which is precipitated rapidly on pouring the above-mentioned clear solution into water, is also optically inactive when dissolved in alcohol. In each case the separated base showed the melting point of the pure triazine, namely, 198°.

2:3-Diphenyl-2:3-dihydro-1:3:4-naphthaisotriazine Picrate.

On adding an acetone solution of picric acid to a suspension of either of the salts *lB,dA* or *dB,dA* in acetone, a clear solution is first obtained, from which a crystalline deposit of the picrate of the base separates on keeping; the substance crystallises in bright, straw-yellow needles, melting at 190—192°:

0.0657 gave 0.1489 CO₂ and 0.0220 H₂O. C=61.8; H=3.6.

C₂₃H₁₇N₃,C₆H₃O₇N₃ requires C=61.7; H=3.5 per cent.

The picrate was also obtained by adding picric acid to an alcoholic solution of either of the two optically active salts.

The various samples of picrate prepared by the two methods, just as the specimens of the free base, proved optically inactive in acetone or alcohol solutions.

Although neither the free base nor its picrate could be obtained in an optically active form, it seems impossible to doubt that the two optically active salts described above contain the *lævo*- and *dextro*-rotatory components respectively of the externally compensated triazine. It is, however, desirable to quote the results of several experiments confirming the conclusion that a resolution of the base has been effected.

On treating equal weights of the two salts, *lB,dA* and *dB,dA*, separately with water, adding the amount of standard sodium hydroxide solution requisite to displace the base completely, and making up to a standard volume, solutions are obtained which have the same rotatory power. The two salts therefore contain the same proportion of the optically active acid, and the difference between their specific rotatory powers must again be attributed to the different optical activity of the bases present.

Further, on dissolving equivalent quantities of the externally compensated base and *d-α*-bromocamphor- π -sulphonic acid in acetic

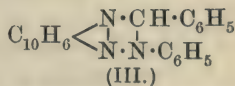
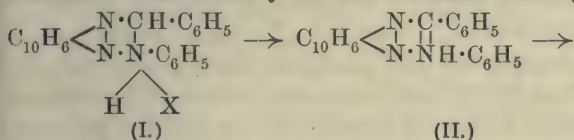
acid and making the volume up to 30 c.c. with the same solvent, the following rotations were obtained:

0.0575 gram of acid and 0.0621 gram of base in 30 c.c. of acetic acid solution:

	Hg, 5461.	Hg, 5780.	Na, 5893.
α	+0.75°	+0.67	+0.56°
$[\alpha]$	+47.0	+42.0	+33.0
$[M]$	+304	+271	+213

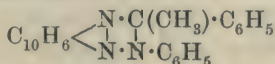
These values lie between those obtained in the same solvent for the two pure salts, and indicate, as was to be expected from the greater solubility of the salt, dB, dA , that the latter substance was not obtained free from the isomeric salt. Since the salt dB, dA has the molecular rotatory power +222° for Hg 5461 in acetic acid and the equimolecular mixture just dealt with gives the value +304°, it follows that the salt dB, dA should have the molecular rotatory power +386° under similar conditions; the value actually obtained was +344°, so that the preparation of the salt dB, dA contained about 5 per cent. of lB, dA .

The extreme facility with which optical inversion occurs during the liberation of the optically active bases from their salts may be attributed tentatively to the operation of the same kind of cause suggested in connexion with the racemisation of *ac*-tetrahydro- β -naphthylamine and 2-methyldihydroindole under similar conditions. The salts of the triazine may be represented by (I), and on treatment with alkali yield the transient form (II), owing to the



mobility of the hydrogen atom attached to the asymmetric carbon atom; the form (II) is potentially inactive, as it no longer contains an asymmetric carbon atom, and probably reverts immediately to the normal form (III).

If this explanation is correct, it should be possible to obtain a triazine of the constitution:

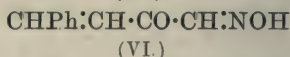
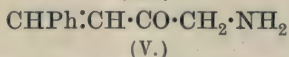
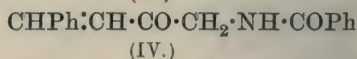
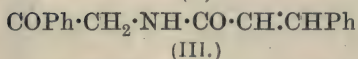
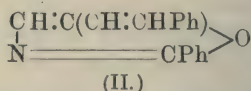
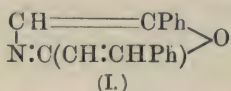


in a stable optically active form.

CXCI.—2-Phenyl-5-styryloxazole.

By ROBINSON PERCY FOULDS and ROBERT ROBINSON.

MINOVICI (*Ber.*, 1896, **29**, 2102) obtained a product melting at 62°, regarded as 5-phenyl-2-styryloxazole (I), by the condensation of benzaldehydecyanohydrin and cinnamaldehyde effected by hydrogen chloride, and in a similar manner Lister and Robinson (*T.*, 1912, **101**, 1303) found that cinnamaldehydecyanohydrin with benzaldehyde yielded a substance melting at about 88°, which might be 2-phenyl-5-styryloxazole (II). Since, however, the latter authors (*loc. cit.*) proved that 5-phenyl-2-styryloxazole, prepared by the dehydration of ω -cinnamoylaminoacetophenone (III), melts in reality at 106°, and that the product melting at 62° is a mixture, it became desirable to synthesise 2-phenyl-5-styryloxazole also, in order to fix its melting point. Actually, we find that this substance melts at 105°, and can readily be produced by submitting styryl benzoylaminomethyl ketone (IV) to the action of concentrated sulphuric acid:



This amide is obtained by the action of benzoyl chloride and sodium acetate on an acetic acid suspension of the stannichloride of styryl aminomethyl ketone (V), which, in its turn, is prepared by the reduction of styryl oximinomethyl ketone (VI) by means of a solution of stannous chloride in concentrated hydrochloric acid. The yields at all stages are excellent.

EXPERIMENTAL.

Salts of Styryl Aminomethyl Ketone (V).

In order to obtain satisfactory yields of styryl oximinomethyl ketone it was found necessary to modify Claisen and Manasse's process (*Ber.*, 1889, **22**, 529), and the following procedure was ultimately adopted: Styryl methyl ketone (5 grams) was dissolved in light petroleum (b. p. 50–60°, 100 c.c.), and gradually treated with freshly distilled *isoamyl* nitrite (12 grams) and concentrated hydrochloric acid (2 c.c.). The temperature was not allowed to rise above 20°, and after allowing to remain for three hours the

oximino-derivative which had crystallised from the solution was collected.

Styryl Aminomethyl Ketone Stannichloride.—Finely powdered styryl oximinomethyl ketone (10 grams) was stirred with a solution of stannous chloride (30 grams) in concentrated hydrochloric acid (70 c.c.). After remaining overnight the crystalline precipitate was collected on a platinum cone, washed with concentrated hydrochloric acid, and dried in the air on porous porcelain. This stannichloride is soluble in hot water or methyl alcohol, but separates in prismatic crystals when hydrochloric acid is added to its solution in these solvents. This crystallisation is, however, always accompanied by a certain amount of decomposition, so that satisfactory analytical results were never obtained.

Platinichloride.—Hydrogen sulphide was passed into a solution of the above stannichloride in hot dilute hydrochloric acid for such a length of time that the tin was almost, but not quite, completely precipitated as sulphide. The platinichloride separated on the addition of platinic chloride to the filtered solution, and was obtained in orange-yellow needles by crystallisation from dilute hydrochloric acid:

0.1420 gave 0.0395 Pt. $Pt = 27.8$.

$(C_{10}H_{11}ON)_2H_2PtCl_6$ requires $Pt = 26.6$ per cent.

This derivative is sparingly soluble, and, when heated, begins to decompose at 190° .

Picrate.—Aqueous picric acid was added to the solution of the hydrochloride obtained as above by eliminating tin from the solution of the stannichloride. The copious, yellow precipitate was collected, and crystallised from methyl alcohol, in which it is rather sparingly soluble. The long, yellow needles so obtained melt and decompose at 167° :

0.1665 gave 0.3018 CO_2 and 0.0541 H_2O . $C = 49.4$; $H = 3.6$.

$C_{10}H_{11}ON, C_6H_3O_7N_3$ requires $C = 49.2$; $H = 3.6$ per cent.

Styryl Benzoylaminomethyl Ketone (IV).

Styryl aminomethyl ketone stannichloride (10 grams) was suspended in glacial acetic acid (50 c.c.), and, together with benzoyl chloride (10 grams) and fused sodium acetate (20 grams), heated on the steam-bath during a quarter of an hour. Dilute hydrochloric acid was then added, and the liquid extracted with a large volume of ether. The ethereal solution was washed with dilute aqueous sodium hydroxide and much water, dried, and at the same time treated with animal charcoal, filtered, and evaporated to small bulk. The benzoyl compound crystallised from the solution, and

was purified by recrystallisation from methyl alcohol. It occurs in long, glistening needles, melting at 121° , and is sparingly soluble in ether, cold benzene, or alcohol:

0.1316 gave 0.3707 CO_2 and 0.0686 H_2O . $\text{C}=76.8$; $\text{H}=5.8$.

$\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}$ requires $\text{C}=77.0$; $\text{H}=5.7$ per cent.

2-Phenyl-5-styryloxazole (II).

The above amide (2 grams) dissolved readily in concentrated sulphuric acid (10 c.c.), and the reaction was complete after allowing the solution to remain during three minutes.

Water and ammonia were added to the liquid, and the precipitated oxazole after collection was crystallised from light petroleum (b. p. 70°). The colourless, prismatic needles melted at 105° :

0.1358 gave 0.4116 CO_2 and 0.0665 H_2O . $\text{C}=82.7$; $\text{H}=5.4$.

$\text{C}_{17}\text{H}_{13}\text{ON}$ requires $\text{C}=82.6$; $\text{H}=5.3$ per cent.

The substance is, for a compound of this type, unusually sparingly soluble in boiling light petroleum, but very readily so in ether, alcohol, or benzene. Its solution in light petroleum exhibits intense blue fluorescence, and this property is also apparent in the solid, which has the appearance of triphenylmethane. A mixture of the two phenylstyryloxazoles could not be separated by crystallisation from light petroleum. The apparently homogeneous substance melted at about 90° , and it is accordingly probable that when cinnamaldehydecyanohydrin and benzaldehyde are condensed by means of hydrogen chloride the formation of 2-phenyl-5-styryloxazole is accompanied by that of 5-phenyl-2-styryloxazole, due, possibly, to a reaction between the cyanohydrin and the aldehyde resulting in the production of a certain amount of benzaldehydecyanohydrin and cinnamaldehyde.

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CXCII.—*The Action of Magnesium Aryl Haloids on Glyoxal.*

By HENRY WREN and CHARLES JAMES STILL.

ALTHOUGH a considerable number of methods are available for the preparation of hydrobenzoin and isohydrobenzoin and their homologues, the members of this group are still somewhat difficult to obtain, and it therefore appeared of sufficient interest to investi-

gate the action of Grignard's reagents on glyoxal in the hope of securing a convenient method of preparing the symmetrically substituted hydro- and *isohydro*-benzoin.

Finely-divided commercial glyoxal, however, is not attacked by prolonged boiling with an ethereal solution of magnesium phenyl bromide, nor is appreciably greater success attained when the ether is replaced by toluene and the mixture heated at 100° during several hours.

Harries and Temme (*Ber.*, 1907, **40**, 165) have shown that when an intimate mixture of commercial glyoxal and phosphoric oxide is heated, yellowish-green vapours of unimolecular glyoxal are evolved, which, when strongly cooled, form a yellow solid that can be preserved if moisture is carefully excluded. For our purpose the isolation of this substance in the solid state has not been necessary, it being found sufficient to dissolve the vapours in anhydrous ether cooled in a mixture of ice and salt, and to add this solution to a cold ethereal solution of the requisite Grignard's reagent. Reaction then occurs readily, with the formation of the desired products.

The conversion of glyoxal into a symmetrically substituted glycol containing two asymmetric carbon atoms can, theoretically, lead to the formation of a mixture of the inactive and racemic forms of the latter. In practice, this does not appear to be the case. Magnesium phenyl bromide and glyoxal yield *isohydrobenzoin*, which can readily be obtained in a state of purity by crystallising the crude product of the reaction from water; since the isomeric *i*-hydrobenzoin is the more sparingly soluble of the two substances in this solvent, it follows that the latter can only be present, at most, in relatively small amount, whilst, further, attempts to isolate it from the residue left after removal of *isohydrobenzoin* from the reaction product were uniformly unsuccessful. Similarly, only one product appears to be formed by the action of magnesium *o*-tolyl bromide on glyoxal. In the case of magnesium *p*-tolyl bromide, however, the difficulty experienced in isolating a compound of constant melting point seems to point to the formation of a mixture of the two isomerides. All attempts to isolate the second form were, however, unsuccessful. In this connexion it is interesting to note that the formation of only one of two possible isomerides is frequently encountered with this class of substance; thus, Irvine and Weir (*T.*, 1907, **91**, 1390) obtained an 85 per cent. yield of hydrobenzoin and only a trace of *isohydrobenzoin* by reducing a solution of benzoin in wet ether with sodium amalgam, whilst McKenzie and Wren (*T.*, 1910, **97**, 475) found that only one form of *l*- $\alpha\beta$ -dihydroxy- $\alpha\beta$ -diphenylpropane and of the corresponding inactive

compound is produced by the action of magnesium methyl iodide on *l*-benzoin and *r*-benzoin respectively.

EXPERIMENTAL.

Preparation of isoHydrobenzoin.

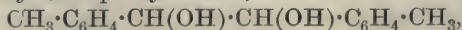
A well-cooled ethereal solution of unimolecular glyoxal was added in small portions at a time to excess of a cold ethereal solution of magnesium phenyl bromide. A vigorous action occurred, which was completed by gently warming the mixture on the water-bath during half-an-hour. The oily product was decomposed by addition of ice and dilute sulphuric acid, and repeatedly extracted with ether. After removal of the latter, the residue was distilled in a current of steam to remove diphenyl. The oil remaining in the flask was dissolved in a considerable volume of boiling water. On cooling, the solution deposited long, colourless needles, which contained water of crystallisation. After being dried in a vacuum over sulphuric acid, the product melted at 117·5—118·8°, whereas Forst and Zincke (*Annalen*, 1876, **182**, 279) give 119—120°. (Found, C=78·36; H=6·61. $C_{14}H_{14}O_2$ requires C=78·50; H=6·54 per cent.)

The identity of the product was further established by converting it into the corresponding diacetate, which, after crystallisation from light petroleum (b. p. 70—80°) and subsequently from methyl alcohol, melted at 117—117·5°. A portion of the substance was dissolved in cold ethyl alcohol, and the solution allowed to evaporate at the ordinary temperature. The residue melted at 116·5—118° initially, but, after re-solidification, at 105—106°, in agreement with the data of Forst and Zincke (*Annalen*, 1876, **182**, 283).

Action of Magnesium p-Tolyl Bromide on Glyoxal.

The reaction was carried out in precisely the same manner as with magnesium phenyl bromide. The crude product, after removal of 4:4'-dimethyldiphenyl, was crystallised from boiling methyl alcohol, whereby a non-homogeneous crop was obtained, the main portion (m. p. 136—150°) being intermixed with small, yellow crystals (m. p. 152—155°). The latter were readily removed, but could not be further investigated owing to lack of material. The main portion was repeatedly crystallised from methyl alcohol or benzene, whereby, ultimately, a product of constant melting point, 161·8—162·6°, was obtained.

αβ-Dihydroxy-αβ-di-p-tolyloethane,



separates from boiling methyl alcohol, in which it is freely soluble, in colourless needles. It dissolves readily in boiling benzene, sparingly in the cold solvent. In boiling water it is sparingly soluble, separating on cooling in fine needles. It dissolves freely in cold acetone or in warm chloroform, sparingly in boiling light petroleum (b. p. 70—80°):

0.1748 gave 0.5067 CO₂ and 0.1155 H₂O. C=79.07; H=7.39.

C₁₆H₁₅O₂ requires C=79.30; H=7.48 per cent.

The corresponding *diacetyl* derivative was prepared by boiling $\alpha\beta$ -dihydroxy- $\alpha\beta$ -di-*p*-tolylethane (2 grams) with acetic anhydride (20 c.c.) during two hours. After removal of excess of the latter on the water-bath, the residue was crystallised from boiling light petroleum (b. p. 70—80°), from which it separated in colourless, stellar aggregates, melting at 105—106°, after slight softening at 103—104°. It is freely soluble in cold chloroform or acetone and in warm methyl alcohol. When a solution of it in cold ethyl alcohol is allowed to evaporate at the ordinary temperature, the residue, both initially and after re-solidification, has the same melting point as the original substance:

0.1711 gave 0.4623 CO₂ and 0.1021 H₂O. C=73.7; H=6.68.

C₂₀H₂₂O₄ requires C=73.56; H=6.81 per cent.

Action of Magnesium o-Tolyl Bromide on Glyoxal.

The action was carried out in precisely the same manner as described in the preceding cases. The product was dissolved in a large quantity of boiling water, from which it separated, on cooling, in long, colourless needles.

$\alpha\beta$ -Dihydroxy- $\alpha\beta$ -di-*o*-tolylethane is sparingly soluble in boiling water or light petroleum, and readily so in cold ethyl and methyl alcohols, acetone, chloroform, or benzene. It melts at 116.5—118°:

0.1790 gave 0.5181 CO₂ and 0.1174 H₂O. C=78.93; H=7.33.

C₁₆H₁₈O₂ requires C=79.30; H=7.48 per cent.

The corresponding *diacetyl* derivative was prepared by means of acetic anhydride in the manner described for the analogous di-*p*-compound. It separates from methyl alcohol in colourless prisms, melting at 99—100° after slight softening at 98.5°. It is freely soluble in the usual organic media, with the exception of light petroleum:

0.2042 gave 0.5491 CO₂ and 0.1210 H₂O. C=73.35; H=6.63.

C₂₀H₂₂O₄ requires C=73.56; H=6.81 per cent.

CXCIII.—*The Mutual Solubilities of Ethyl Acetate and Water and the Densities of Mixtures of Ethyl Acetate and Ethyl Alcohol.*

By RICHARD WILLIAM MERRIMAN.

A KNOWLEDGE of the mutual solubilities of ethyl acetate and water at ordinary atmospheric temperatures was required for the work on the azeotropic mixtures of these liquids described in the succeeding paper.

The solubility of water in ethyl acetate is easily determined. Known quantities of the ester and water are mixed in a vessel provided with a ground-in stopper carrying a thermometer. The mixture is then warmed until a clear solution is formed, and then slowly cooled until a slight general cloudiness begins to form. The cloudy mixture is then slowly warmed, with frequent shaking, until a clear solution is obtained. The "cloudy point" is the mean of these two observations. The "cloudy point" is determined several times for each mixture. This method gives accurate results when the solubility varies only to a small extent with the temperature.

The solubility of ethyl acetate in water cannot be conveniently determined in a similar manner. The solubility decreases with rise of temperature, so that a clear solution would have to be warmed in order to find the cloudy point, and the cloudy mixture cooled in order to obtain a clear solution. This cloudy point cannot be found as accurately as when the ester is in excess, the difference between the temperatures of clouding and clearing up being greater.

A different method was therefore used. A bulb of 75 c.c. capacity was sealed on to a tube divided into tenths of a c.c. Known weights of water and ethyl acetate were introduced into the apparatus, and the end of the tube sealed up. It was then placed in a thermostat and shaken until the two layers of liquid were thoroughly saturated. This point is reached when the volume of each layer, after it has completely separated out, has a constant value.

The weight of the aqueous layer is calculated by multiplying its volume by the density of water saturated with ester at the temperature of the thermostat. The weight of the ester layer is calculated in a similar manner. The sum of the two weights thus

calculated should equal the total weight of water and ester taken. We thus have, at each temperature, an absolute check on the accuracy of all the quantities used in the calculations.

The amount of water dissolved in the ester layer is known. We therefore know the quantities of water and ester in the aqueous layer, and can calculate the solubility of the ester in the water. The amount of ester started with should be arranged so that the volume of the ester layer is never more than is necessary to get a clear separation of the two layers. In this way a small error in the determination of the solubility of water in the ester by the cloudy-point method would be negligible. By suitably altering the shape of the closed vessel the method could be used for accurately determining the solubility of water in the ester. In this case the aqueous layer would have to be of small volume. This laborious process is unnecessary in the case of ethyl acetate, as water is only moderately soluble in it, and the cloudy-point method gives sufficiently accurate results. When dealing with two liquids which are fairly readily soluble in each other, the following series of experiments would be carried out. The approximate solubilities for both liquids would first be determined by the cloudy-point method. Then the accurate value would be found by the method here described, in one case having a small upper layer and in the other case a small lower layer.

I.—*The Solubility of Water in Ethyl Acetate.*

The apparatus used in finding the "cloudy points" of mixtures of ethyl acetate and water consisted of a stout glass bottle holding about 150 c.c. The stopper was very accurately ground in, and was provided with lugs by which it could be securely wired in position. A thermometer was fused to the stopper, the whole of the stem being inside the bottle. The bottle was filled with dry air and weighed. About 100 grams of ethyl acetate, prepared and purified in the manner previously described (Wade and Merriman, T., 1912, 101, 2429), were introduced into the bottle and weighed, the weight being reduced to a vacuum. The required amount of water was then added and weighed.

The stopper was wired on and the bottle shaken and warmed, when necessary, until a clear solution was obtained. The solution was then allowed to slowly cool, with frequent shaking, in a vessel placed in a thermostat kept at a temperature a little below the cloudy temperature, and the temperature was observed when a slight cloudiness formed throughout the solution. The solution

was then warmed and the temperature at which the mixture cleared was noted. Consecutive readings did not differ by more than 0.1° , corresponding with an error of less than 0.01 per cent. in the solubility of the water in the ester. A fresh mixture was made up for each determination.

The experimental results are given in table I. They lie on a smooth curve, shown in Fig. 2. The increment in solubility, per degree rise in temperature, increases with the temperature. The percentages of water in saturated ester for even temperatures were read from this curve, and are given in table II. The amounts of water dissolved by 100 grams of the ester are given in the same table.

TABLE I.

Temperature.	Percentage of water in saturated ester.	Temperature.	Percentage of water in saturated ester.
1.6°	2.36	36.7°	3.72
7.1	2.51	39.6	3.90
13.3	2.71	40.7	3.94
17.7	2.90	46.0	4.22
20.0	2.96	53.1	4.62
25.9	3.26	58.0	4.90
33.4	3.60		

TABLE II.

Temperature.	Percentage of water in saturated ester.	Water dissolved by 100 grams of ester. Grams.
0°	2.28	2.34
5	2.44	2.50
10	2.61	2.68
15	2.79	2.87
20	2.98	3.07
25	3.19	3.30
30	3.42	3.54
35	3.66	3.80
40	3.92	4.08
45	4.19	4.37
50	4.46	4.67
55	4.74	4.98
60	5.02	5.29

II.—*The Densities of Water Saturated with Ethyl Acetate.*

When water is shaken with ethyl acetate a cloudy mixture is obtained if the ester is in slight excess. On cooling such a cloudy mixture it clears because the solubility of the ester increases with fall of temperature. The only method by which the densities of cloudy solutions may be accurately determined is by the use of a Westphal balance. The presence of a fine suspension in a liquid will not affect the upthrust on a body immersed in the liquid so

long as none of the suspension is actually sticking to the immersed body.

A carefully calibrated Westphal balance provided with an agate knife edge is an instrument by means of which densities may be determined with certainty within ± 0.0001 after a little practice. Long experience with a carefully selected Westphal balance has proved its value for work in which the highest accuracy is unnecessary.

The following method was used in determining the density of water saturated with ester at any temperature.

A mixture of water and ester is made up, which will become cloudy on warming to the required temperature. The mixture is cooled several degrees below this temperature, so that a clear solution is formed. The solution is placed in a test-tube, and the plummet of the Westphal balance suspended in it. The test-tube must be wide enough to permit the use of a stirrer made of platinum wire bent into a ring at the end, which can be moved up and down the tube without touching the cylindrical plummet. The test-tube is placed in a wider tube containing water at a temperature a little above the temperature at which the solution becomes cloudy.

The instrument is approximately adjusted by means of the riders, and the solution continually stirred. The temperature of the solution gradually rises, and the riders are moved to preserve the balance. As soon as a slight cloudiness appears throughout the liquid, the stirring is stopped, the exact adjustment made, and the temperature read. The plummet is itself a thermometer, which must be standardised before use.

The outside test-tube is now replaced by a tube containing water a little colder than the temperature at which the solution becomes clear. Stirring is re-started, and the solution allowed slowly to cool. Just before it is absolutely clear the stirring is stopped, the riders are adjusted, and the temperature is read.

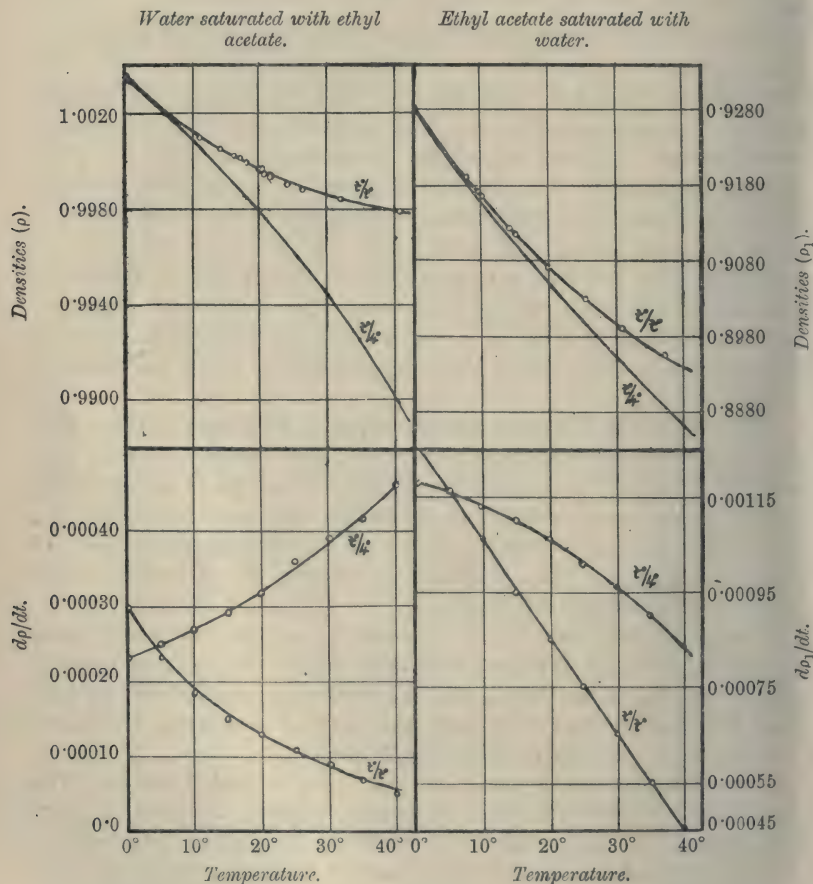
The estimation was repeated several times in each direction. The temperatures recorded were, of course, slightly different in each determination. Each result was corrected to a mean temperature, and the mean value of the reading of the riders was recorded.

The reading of the riders for distilled water at the same temperature was determined immediately before and after the experiment with the solution. The results obtained are given in table III. They lie very close to a smooth curve, shown in Fig. 1. From this curve the values at regular intervals of temperature were read, and are given in table IV, together with the densities com-

pared with water at 4° . The latter values lie on a smooth curve, also drawn in Fig. 1, of a different type from the curve of densities at t°/t° . It will be noticed that water saturated with ethyl acetate possesses no point of maximum density above 0° .

The rate of change of density with the temperature, dp/dt , for

FIG. 1.



each curve is shown in Fig. 1. Although these first difference curves are deduced from smoothed density curves, the points do not lie exactly on them, but the general trend of each curve is indicated. Densities must be known with an accuracy of ± 0.00001 to produce a smooth first-difference curve.

TABLE III.

Densities of Water Saturated with Ethyl Acetate.

Temperature.	Reading for water saturated with ester.	Reading for water.	Density of water saturated with ester at t°/t° .
0.0°	1.0023	0.9988	1.0035
6.1	1.0010	0.9990	1.0020
11.5	0.9997	0.9983	1.0009
14.5	0.9991	0.9986	1.0005
16.4	0.9986	0.9984	1.0002
17.05	0.9985	0.9984	1.0001
18.0	0.9982	0.9982	1.0000
20.0	0.9977	0.9980	0.9997
20.4	0.9978	0.9980	0.9998
20.65	0.9975	0.9979	0.9996
22.0	0.9972	0.9976	0.9996
22.05	0.9971	0.9976	0.9995
24.3	0.9963	0.9972	0.9991
26.1	0.9957	0.9968	0.9989
32.5	0.9937	0.9952	0.9985
40.3	0.9905	0.9426	0.9979

TABLE IV.

Densities of Water Saturated with Ethyl Acetate read from the Experimental Curve.

Temperature.	Density t°/t° . (P_1)	dp/dt .	Density $t^{\circ}/4^{\circ}$. (P_1 .)	dp_1/dt .
0°	1.0035	0.00030	1.0034	0.00023
5	1.0022	0.00023	1.0022	0.00025
10	1.0012	0.00018	1.0009	0.00027
15	1.0004	0.00015	0.9995	0.00029
20	0.9997	0.00013	0.9979	0.00032
25	0.9991	0.00011	0.9962	0.00036
30	0.9986	0.00009	0.9943	0.00039
35	0.9982	0.00007	0.9923	0.00042
40	0.9979	0.00005	0.9901	0.00046

III.—*The Densities of Ethyl Acetate Saturated with Water.*

These densities were determined by means of the Westphal balance as described in the previous section. Water is added to ethyl acetate so as to produce a cloudy solution at the required temperature. The mixture is warmed until the cloudiness disappears, and the plummet of the Westphal balance is suspended in it. The test-tube containing the solution is surrounded by water at a temperature slightly below the cloudy point. The solution is slowly cooled, and just as cloudiness commences the riders are adjusted as previously described. The outer jacket is then filled with water at a slightly higher temperature than the cloudy point, and the solution allowed to become warm, with constant stirring, until it just becomes clear again, and the riders are then adjusted.

The experimental results are given in table V, and are represented graphically in Fig. 1. The values at even temperatures given in table VI were read from this curve, and the densities, compared with water at 4°, calculated from them. These calculated values lie on a curve, drawn in Fig. 1, of a similar character to the $D\ t^{\circ}/t^{\circ}$ curve. The curves showing the rate of change of the two series of densities, with the temperature, are also drawn in Fig. 1.

TABLE V.

Densities of Ethyl Acetate Saturated with Water.

Temperature.	Reading for ester saturated with water.	Reading for water.	Density of ester saturated with water at t°/t° .
0.0°	0.9269	0.9988	0.9281
6.8	0.9190	0.9990	0.9200
7.8	0.9180	0.9990	0.9190
9.6	0.9162	0.9989	0.9173
10.3	0.9158	0.9989	0.9169
13.3	0.9120	0.9987	0.9133
15.1	0.9102	0.9986	0.9116
20.0	0.9052	0.9980	0.9072
25.1	0.9000	0.9970	0.9030
31.0	0.8946	0.9956	0.8990
38.1	0.8885	0.9934	0.8951

TABLE VI.

Densities of Ethyl Acetate Saturated with Water read from Smooth Curve.

Temperature.	Density t°/t° . (P_1)	dp/dt .	Density $t^{\circ}/4^{\circ}$. (P_1)	dp_1/dt .
0°	0.9281	0.00126	0.9280	0.00118
5	0.9222	0.00116	0.9222	0.00116
10	0.9167	0.00106	0.9164	0.00113
15	0.9117	0.00095	0.9108	0.00110
20	0.9072	0.00085	0.9054	0.00106
25	0.9031	0.00075	0.9002	0.00101
30	0.8996	0.00065	0.8953	0.00096
35	0.8966	0.00055	0.8907	0.00090
40	0.8941	0.00045	0.8863	0.00084

IV.—*The Solubility of Ethyl Acetate in Water.*

The apparatus has already been described in the introduction. The graduated tube was calibrated to give a correct reading of the volume at 10°.

79.47 Grams of water were introduced into the apparatus at a temperature of 10°. The meniscus stood at the 3.05 c.c. mark. The weight of water corrected to a vacuum was 79.556 grams. Therefore its volume at 10° was 79.58 c.c., and hence the volume of the bulb to the zero mark was 76.53 c.c. at a temperature of 10°.

12.13 Grams of ethyl acetate were added, and the apparatus was sealed up. The corrected weight of the ester was 12.146, so that the total weight was 91.702 grams. The apparatus was then placed in a thermostat and shaken for one hour. It was then fixed in the thermostat in a vertical position, and the two layers were allowed to separate out. The readings of the top of the ester layer and of the line of separation were then taken. The shaking was renewed for another thirty minutes, and the readings were made once more. The process was continued until constant readings were obtained. Saturation of both layers was always complete in less than two hours. The readings are given in table VII.

TABLE VII.

Temperature.	Reading of top of aqueous layer.	Reading of top of ester layer.
	c.c.	c.c.
0.0°	11.60	15.19
4.0	11.15	15.27
8.1	10.68	15.41
12.3	10.28	15.58
15.0	10.02	15.70
15.5	10.03	15.69
15.6	10.00	15.70
17.4	9.90	15.78
20.4	9.70	15.86
27.0	9.40	16.11
27.4	9.38	16.15
30.5	9.27	16.27
31.6	9.24	16.36
40.5	9.11	16.79

The volume of each layer was then calculated, the values obtained being given in table VIII.

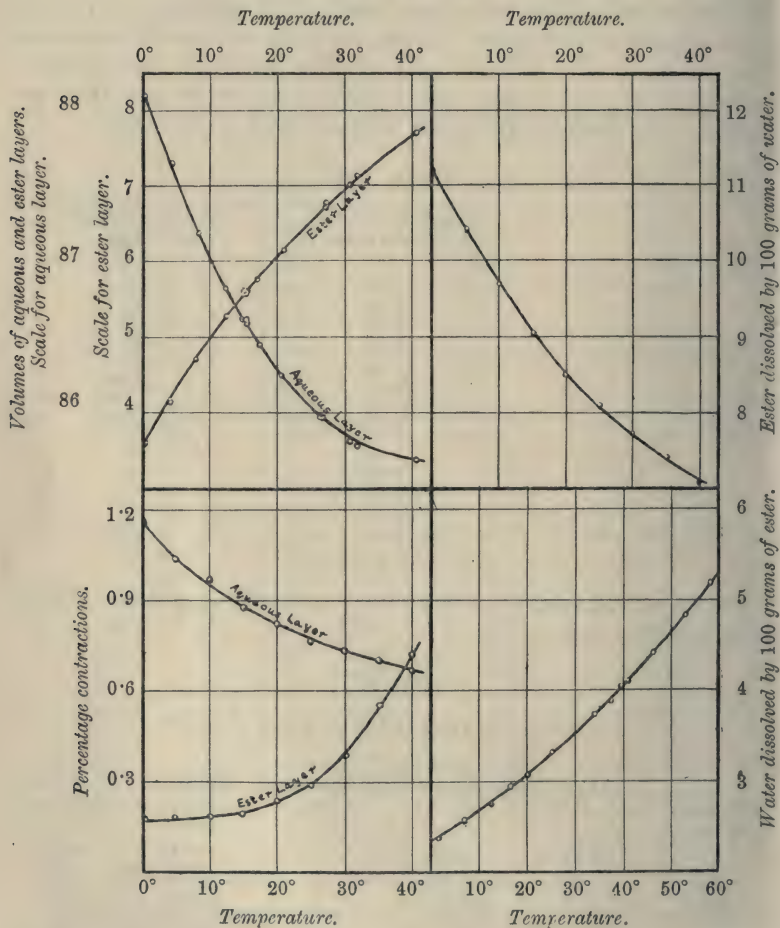
TABLE VIII.

Volumes of Aqueous and Ester Layers.

Temperature.	Volume of bulb at 10°.	Reading of top of aqueous	Correction for expansion	Volume of aqueous layer.	Volume of ester layer.
		layer. c.c.	of glass. c.c.		
0.0°	76.53	11.60	-0.02	88.11	3.59
4.0	76.53	11.15	-0.01	87.67	4.12
8.1	76.53	10.68	0.00	87.21	4.73
12.3	76.53	10.28	0.00	86.81	5.30
15.0	76.53	10.02	+0.01	86.56	5.68
15.5	76.53	10.03	0.01	86.57	5.66
15.6	76.53	10.00	0.01	86.54	5.70
17.4	76.53	9.90	0.01	86.44	5.88
20.4	76.53	9.70	0.02	86.25	6.16
27.0	76.53	9.40	0.04	85.97	6.71
27.4	76.53	9.38	0.04	85.95	6.77
30.5	76.53	9.27	0.04	85.84	7.00
31.6	76.53	9.24	0.04	85.81	7.12
40.5	76.53	9.11	0.06	85.70	7.68

The volumes of each layer are plotted against the temperatures in the curves in Fig. 2. From the ester layer curve the values given in column (a) of table IX were read. These volumes were multiplied by the density of the ester saturated with water at $t^{\circ}/4^{\circ}$

FIG. 2.



taken from table VI. The weights of the ester layer thus obtained are given in column (b) of table IX. The percentages of water in the saturated ester, given in column (c), are taken from table II. The values given in columns (d), (e), and (f) were then calculated.

TABLE IX.

Tem- perature.	(a) Volume of saturated ester. c.c.	(b) Weight of saturated ester. Grams.	(c) Percentage of water.	(d) Weight of water. Gram.	(e) Weight of ester. Grams.	(f) Weight of ester in the aqueous layer. Grams.
0°	3.59	3.33	2.28	0.076	3.25	8.90
5	4.30	3.97	2.44	0.097	3.87	8.28
10	5.00	4.59	2.61	0.12	4.47	7.68
15	5.61	5.11	2.79	0.14	4.97	7.18
20	6.11	5.55	2.98	0.16	5.39	6.76
25	6.57	5.91	3.19	0.19	5.72	6.43
30	6.97	6.25	3.42	0.21	6.04	6.11
35	7.31	6.52	3.66	0.24	6.28	5.87
40	7.65	6.78	3.92	0.27	6.51	5.64

Table X was constructed in a similar way. The final results for the solubility of ethyl acetate in water are given in columns (d) and (e). The volumes of the aqueous layer in column (a) were read from the smoothed curve given in Fig. 2. The corresponding weights were calculated by multiplying by the density at $t^{\circ}/4^{\circ}$ taken from table IV. Column (c) is copied from column (f) of table IX. Hence the values given in columns (d) and (e) were readily calculated.

TABLE X.

Temper- ature.	(a) Volume of water saturated with ethyl acetate. c.c.	(b) Weight of water saturated with ester. Grams.	(c) Weight of dissolved ester. Grams.	(d) Percentage of ethyl acetate in saturated water.	(e) Weight of ethyl acetate in 100 grams of water. Grams.
0°	88.11	88.41	8.90	10.08	11.21
5	87.54	87.73	8.28	9.44	10.40
10	87.02	87.10	7.68	8.82	9.68
15	86.58	86.54	7.18	8.30	9.06
20	86.28	86.10	6.76	7.85	8.51
25	86.05	85.72	6.43	7.50	8.11
30	85.87	85.38	6.11	7.17	7.74
35	85.76	85.10	5.87	6.90	7.40
40	85.70	84.85	5.64	6.65	7.13

The values given in column (e) are plotted against the temperatures in Fig. 2. They lie on an extremely smooth curve. The smoothed values are given in table XI.

TABLE XI.

Solubility of Ethyl Acetate in Water.

Temperature.	Percentage of ethyl acetate in saturated water.	Weight of ethyl acetate dissolved by 100 grams of water.	
		Grams.	
0°	10.08	11.21	
5	9.40	10.38	
10	8.81	9.67	
15	8.30	9.05	
20	7.86	8.53	
25	7.48	8.08	
30	7.15	7.71	
35	6.87	7.37	
40	6.63	7.10	

The test of the combined consistency of the whole work, mentioned in the introduction, may now be applied. Column (a) of table XII represents the weights of the aqueous layer, taken from column (b) of table X. Column (b) of table XII represents the weights of the ester layer, taken from column (b) of table IX. The sum of these two weights, given in column (c), should in each case equal the total weight of ethyl acetate and water taken, namely, 91.70 grams. The error is given in column (e), and the percentage error in column (f). The errors are remarkably small, considering that the calculated weights of ethyl acetate and water involve the use of the following determinations: (1) the solubility of water in ethyl acetate, (2) the densities of water saturated with ester, (3) the densities of ethyl acetate saturated with water, and (4) the readings of the volumes of the two layers.

TABLE XII.

Temperature.	(a) Weight of aqueous layer.	(b) Weight of ester layer.	(c) Total weight.	(d) Total weight taken.	(e) Error.	(f) Percentage error.
	Grams.	Grams.	Grams.	Grams.	Gram.	
0°	88.41	3.33	91.74	91.70	0.04	0.044
5	87.73	3.97	91.70		0.00	0.000
10	87.10	4.59	91.69		-0.01	0.011
15	86.54	5.11	91.65		-0.05	0.055
20	86.10	5.55	91.65		-0.05	0.055
25	85.72	5.91	91.63		-0.07	0.076
30	85.38	6.25	91.63		-0.07	0.076
35	85.10	6.52	91.62		-0.08	0.087
40	84.85	6.78	91.63		-0.07	0.076

V.—*Contraction Produced when Water is Saturated with Ethyl Acetate.*

It is at once obvious that a large contraction occurs when water is mixed with the less dense ethyl acetate, because the density of the saturated solution is 1.0034 at $0^{\circ}/4^{\circ}$, corresponding with the relatively enormous contraction of 1.16 per cent. Table XIII gives the percentage contractions at different temperatures. These contractions lie on the smooth curve drawn in Fig. 2.

TABLE XIII.

Contraction Produced on Saturating Water with Ethyl Acetate.

Temperature.	Density of saturated water at $t^{\circ}/4^{\circ}$.	Calculated density.	Difference.	Percentage contraction.
0°	1.0034	0.9919	0.0115	1.16
5	1.0022	0.9919	0.0103	1.04
10	1.0009	0.9913	0.0096	0.97
15	0.9995	0.9908	0.0087	0.88
20	0.9979	0.9898	0.0081	0.82
25	0.9962	0.9886	0.0076	0.77
30	0.9943	0.9871	0.0072	0.73
35	0.9923	0.9854	0.0069	0.70
40	0.9901	0.9836	0.0065	0.66

VI.—*Contractions Produced when Ethyl Acetate is Saturated with Water.*

At the higher temperatures where the solubility of the water becomes appreciable, the percentage contractions approach the values for the aqueous solutions.

TABLE XIV.

Contractions Produced on Saturating Ethyl Acetate with Water.

Temperature.	Density of saturated ethyl acetate at $t^{\circ}/4^{\circ}$.	Calculated density at $t^{\circ}/4^{\circ}$.	Difference.	Percentage contraction.
0°	0.9280	0.9263	0.0017	0.183
5	0.9222	0.9205	0.0017	0.185
10	0.9164	0.9147	0.0017	0.186
15	0.9108	0.9090	0.0018	0.198
20	0.9054	0.9033	0.0021	0.233
25	0.9002	0.8976	0.0026	0.290
30	0.8953	0.8918	0.0035	0.392
35	0.8907	0.8858	0.0049	0.553
40	0.8863	0.8800	0.0063	0.716

These contractions are also represented in Fig. 2 by a smooth curve. The two curves representing the contractions are smooth, and show no points of inflexion or changes of curvature. There is

therefore no evidence of the formation of definite hydrates of ethyl acetate in either of the solutions. Whilst contraction occurs in the formation of both of the saturated solutions, yet the solubility of ethyl acetate in water increases with rise of temperature, but the solubility of water in ethyl acetate decreases with rise of temperature.

VII.—*The Densities of Mixtures of Ethyl Acetate and Ethyl Alcohol.*

When ethyl acetate is mixed with ethyl alcohol a small expansion takes place, accompanied by a fall in temperature. The densities of the mixtures must, therefore, be determined experimentally.

Mixtures of known composition were made up in the following way. A glass bottle, provided with a perfectly fitting ground-in stopper, was filled with dry air and connected with a calcium chloride tower. While still connected with the drying tower it was placed in melting ice for ten minutes. It was then rapidly disconnected from the tower, and the stopper quickly inserted. The bottle was warmed up to the temperature of the balance, and then carefully dried and weighed.

It was again placed in the ice and connected with the drying tower. When cooled to 0° the bottle was rapidly disconnected, a quantity of ice-cold alcohol poured in, and the stopper quickly inserted. The bottle was treated as before and weighed. The weight of alcohol was corrected for the displacement of the dry air at a temperature of 0° .

In a similar way the ethyl acetate was added to the bottle, and its corrected weight found. The two liquids were thoroughly mixed, and the density of the liquid at 0° was determined by the method already described (Wade and Merriman, T., 1912, 101, 2429).

The experimental results are given in table XV. Column (a) gives the percentages of alcohol; column (b) the densities at $0^{\circ}/0^{\circ}$; column (c) the volume of 100 grams of the mixture; column (d) the theoretical volume; and column (e) gives the percentage expansion. The volumes represented in columns (c) and (a) are not absolutely true, as the densities at $0^{\circ}/0^{\circ}$ were used in calculating them, but they are relatively true, so that the percentage expansions are correct. The density of absolute alcohol at $0^{\circ}/0^{\circ}$ was 0.80639; the density of pure ethyl acetate at $0^{\circ}/0^{\circ}$ was 0.92466. These values were the same as those previously obtained (Wade and Merriman, T., 1912, 101, 2434; Merriman, this vol., p. 630).

TABLE XV.

Percentage of alcohol.	Density 0°/0°.	Volume of 100 grams. c.c.	Theoretical volume. c.c.	Percentage expansion in volume.
5.103	0.91746	108.9964	108.9572	0.036
10.184	0.91043	109.8376	109.7631	0.068
15.662	0.90309	110.7306	110.6321	0.089
16.185	0.90237	110.8180	110.7150	0.094
19.920	0.89751	111.4188	111.3075	0.100
24.841	0.89116	112.2138	112.0880	0.112
30.308	0.88428	113.0862	112.9552	0.116
34.588	0.87898	113.7681	113.6341	0.118
41.100	0.87106	114.8021	114.6670	0.118
50.059	0.86045	116.2191	116.0880	0.113
60.511	0.84841	117.8670	117.7459	0.103
71.015	0.83670	119.5170	119.4120	0.088
85.750	0.82088	121.8198	121.7492	0.058
94.654	0.81175	123.1910	123.1616	0.026

The percentage expansions are plotted against the percentages of alcohol in the curve in Fig. 3. The curve was smoothed, and the percentage expansions given in table XVI were read from the smoothed curve.

TABLE XVI.

Percentage Expansions of Mixtures of Ethyl Alcohol and Ethyl Acetate.

Percentage of alcohol.	Percentage expansion.	Percentage of alcohol.	Percentage expansion.
0	0.00	55	0.1091
5	0.0365	60	0.1042
10	0.0656	65	0.0983
15	0.0874	70	0.0911
20	0.1024	75	0.0825
25	0.1120	80	0.0724
30	0.1170	85	0.0600
35	0.1181	90	0.0450
40	0.1177	95	0.0260
45	0.1159	100	0.00
50	0.1130		

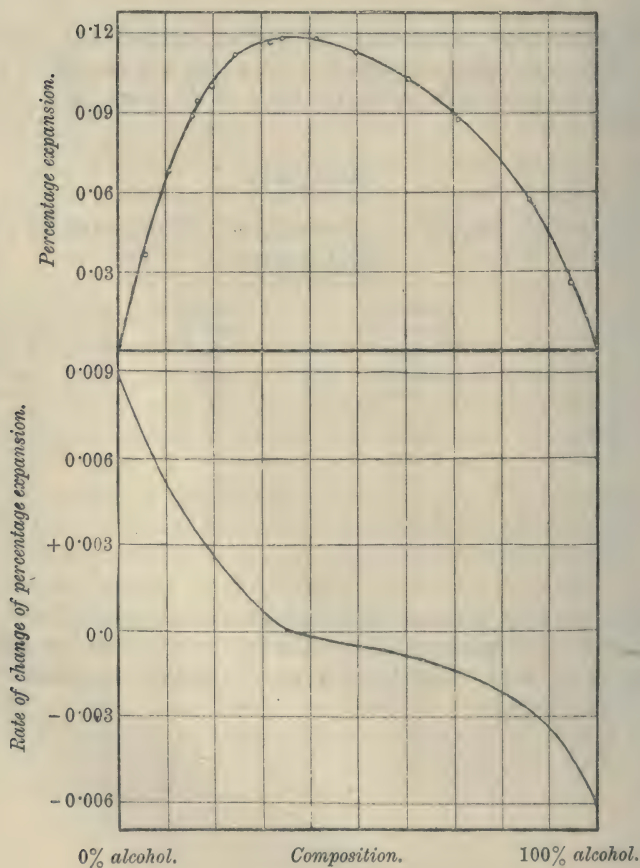
With the help of these smoothed expansions the following table of densities was constructed for use in the work on the azeotropic mixtures of ethyl acetate and ethyl alcohol described in the succeeding paper.

TABLE XVII.

Densities of Mixtures of Ethyl Acetate and Ethyl Alcohol.

Percentage of alcohol.	Density 0°/0°.	Percentage of alcohol.	Density 0°/0°.
0	0·92466	55	0·85471
5	0·91759	60	0·84899
10	0·91070	65	0·84335
15	0·90397	70	0·83780
20	0·89739	75	0·83234
25	0·89095	80	0·82696
30	0·88466	85	0·82167
35	0·87848	90	0·81648
40	0·87239	95	0·81137
45	0·86641	100	0·80639
50	0·86052		

FIG. 3.



It will be seen from the curve in Fig. 3 that the point of maximum expansion corresponds with a mixture containing about 35 per cent. of ethyl alcohol. This mixture contains, as nearly as possible, one molecular proportion of each liquid. This fact might be taken as proving combination between the alcohol and the ester in equimolecular proportions. The expansions, however, are so small that densities would have to be known with absolute accuracy within 0.000001, in order to fix the maximum point with complete certainty. It is obvious that if there is an expansion or contraction for any given mixture, there must be a point of maximum expansion or contraction, and whether the cause be physical or chemical, the maximum expansion or contraction would, no doubt, take place in the mixture containing an equal number of molecules of each liquid.

The curve showing the relation between rate of change of expansion and the composition, given in Fig. 3, has a point of inflexion corresponding with the point of maximum expansion. There is no other point of inflexion, so that there is no evidence of other molecular compounds of ethyl acetate and alcohol.

The composition-density curve is a sagged curve not far removed from a straight line. According to the theoretical deductions of Denison (*Trans. Faraday Soc.*, 1912, **8**, 20), such a curve denotes either dissociation of one or both components or chemical combination between them. Chemical combination has probably taken place if the deviation curve, as in the present instance, reaches a maximum when the components are present in simple molecular proportions; but when the maximum point corresponds with equal molecular proportions, the theory indicates that the molar composition-deviation curve should be symmetrical. This curve is not symmetrical for the present mixture, so that the deviation of the composition-density curve from a straight line is probably due to the dissociation of the associated components, which is also indicated by the fact that the deviation is an expansion accompanied by a fall in temperature.

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CXCIV.—*The Azeotropic Mixtures of Ethyl Acetate, Ethyl Alcohol, and Water at Pressures Above and Below the Atmospheric Pressure. Part I.*

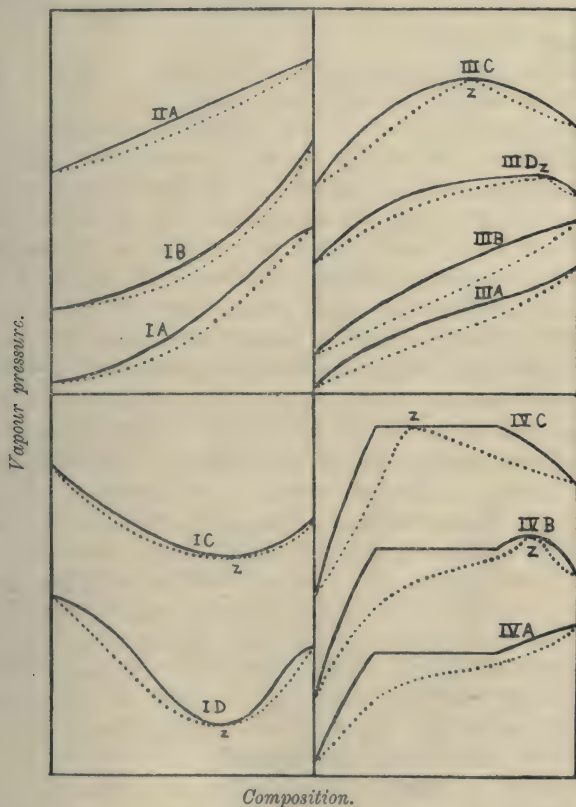
By RICHARD WILLIAM MERRIMAN.

THE most complete account of the possible types of vapour-pressure curves of binary mixtures has been given by Marshall (T., 1906, **89**, 1350). This author, starting from the Duhem-Margules equation: $x d \log p_1 + (1-x) d \log p_2 = 0$, where p_1 , p_2 are the partial pressures of the two substances, and x , $(1-x)$ the molecular proportions of the two substances in the liquid mixture, found that twelve kinds of vapour-pressure curves may occur. These possible types are represented by the curves in Fig. 1, which show the relation between vapour pressure and composition at constant temperature. The composition of the vapour is usually different from that of the liquid, and is represented on the diagrams by the dotted curves. It will be readily seen that mixtures of liquids which give vapour-pressure curves of types 1A, 1B, 2A, 3A, 3B, or 4A can be completely separated from each other by suitable fractional distillation, the vapour, as it rises up the fractionating column, becoming continually richer in the component of higher vapour pressure, whilst the liquid remaining in the flask becomes less rich in this constituent. Liquids which give curves of types 1D, 1C, 4B, 4C, 3C, or 3D cannot be completely separated by fractional distillation. If the curves show a maximum of vapour pressure, an azeotropic mixture (see Wade and Merriman, T., 1911, **99**, 997) of composition Z will distil over as the first fraction. When there is a minimum point an azeotropic mixture will form the last fraction. The shape of the vapour-pressure curve is only of importance when the maximum or minimum point is only slightly below or above the rest of the curve. In this case the azeotropic mixture can only be isolated after several fractionations.

The most important suggestion as to the kind of liquids which form azeotropic mixtures was made by Bancroft ("Phase Rule," p. 119). He there states: "If two consolute liquids have the same vapour pressure at any given temperature, some mixture of the two must have either a maximum or a minimum vapour pressure at that temperature, unless all concentrations have the same value. If at other temperatures the isothermal curve has neither a maximum nor a minimum, it is possible to pass by change of temperature from a system behaving in one way to a system behaving in another. This would prevent any deductions from the form of the pressure

curve at one temperature to that at another. The alternative is that all consolute liquids with intersecting vapour-pressure curves form solutions with a maximum or minimum value at some concentration." Pettit (*J. Physical Chem.*, 1899, **3**, 349) examined the vapour-pressure curves of many pairs of liquids which form azeotropic mixtures, and in nearly all cases the curves cut each other, whilst in the other cases they definitely approached each other

FIG. 1.



within the range of temperatures of the observations. The present author (this vol., p. 635) found that the vapour-pressure curves of ethyl acetate and ethyl alcohol, which form an azeotropic mixture, cross each other. A mixture of ethyl alcohol and water, however, breaks both of Bancroft's rules. In the first place, the vapour-pressure curves of alcohol and water never actually cross each other, although they approach nearer and nearer to each other as the

temperature is reduced to the freezing point of water (Merriman, this vol., p. 936). In the second place, the work of Wade and Merriman (T., 1911, **99**, 997) on the effect of change of pressure on the composition of the azeotropic mixture of ethyl alcohol and water, showed that the vapour-pressure curve must change from type 3C to type 3B, because at pressures below 75 mm. complete separation of ethyl alcohol and water can be effected by fractionation. Schreinemakers (*Zeitsch. physikal. Chem.*, 1900, **35**, 459) also found that the vapour-pressure curves of mixtures of phenol and water changed from type 3C to type 4B as the temperature was lowered from 90° to 60°.

There is no doubt, however, that Bancroft's rule is of considerable use to the organic chemist, who should be always on the lookout for the possibility of the formation of azeotropic mixtures, because constancy of boiling point is no criterion that a pure chemical individual is being dealt with.* The working rule is that any pair of liquids with vapour-pressure curves which definitely approach each other, even if they do not cross at known temperatures, will probably form an azeotropic mixture, provided that the boiling points at the atmospheric pressure are not too far apart.

The vapour-pressure curves of associated liquids, such as water, alcohols, ketones, and acids, are abnormal, and show a tendency to cut the vapour-pressure curves of normal liquids, so that if one of the components of a binary mixture is one of these abnormal liquids, and the boiling points are within 50° of each other, an azeotropic mixture is almost certain to be formed.

Many such mixtures have been discovered since Dalton (Berzelius, *Jahresber.*, 1832, **11**, 71) isolated the azeotropic mixture of hydrochloric acid and water. The earlier workers, with the exception of Roscoe, were of the opinion that the constituents of such mixtures were in molecular proportions. Subsequent investigations (Konowaloff, *Ann. Phys. Chem.*, 1881, [iii], **14**, 34; Young and Fortey, T., 1902, **81**, 717; Homfray, T., 1905, **87**, 1441) indicated that the position of the maximum or minimum point of a vapour-pressure curve altered with the pressure.

The azeotropic mixtures of ethyl acetate, ethyl alcohol, and water have been studied at the ordinary pressure by Wade (T., 1905, **87**, 1656). The present investigation extends the observations from 25 mm. to 1500 mm. pressure, with the object of systematically following the alteration in composition of the azeotropic mixtures

* In this connexion, Ostwald ("Outlines of General Chemistry," p. 313) points out that if a liquid distils at a constant temperature without change of composition, and freezes at a constant temperature without change of composition, we can safely assume that it is a chemical individual.

with change of pressure. Similar work has already been carried out in the case of ethyl alcohol and water (Wade and Merriman, *loc. cit.*), and it was hoped that a comparison of several cases would evolve an empirical rule relating to the change of composition of a binary azeotropic mixture of minimum boiling point, with alteration of pressure. Another object of the investigation was to see if there were any indications of the transition of an azeotropic mixture or temporary hylotropic substance into a substance which can form hylotropic phases within a finite range of temperatures and pressures, the possibility of which has been discussed by Ostwald (Faraday Lecture, T., 1904, 85, 516).

I.—*The Azeotropic Mixtures of Ethyl Acetate and Water from 50 mm. to 1450 mm. Pressure.*

The ethyl acetate was purified in the manner recently described (Wade and Merriman, T., 1912, 101, 2429). The distillations were carried out with the apparatus used for the azeotropic mixtures of ethyl alcohol and water (T., 1911, 99, 997). The temperatures recorded are on the hydrogen scale, and the pressures have been reduced to 0° in the latitude of Paris. The following detailed account of the determination of the composition of the azeotropic mixture formed at 446.2 mm. will explain the method used.

A. *Ester in Excess.*

Ethyl acetate, 67.93 grams; water, 2.51 grams.

Fraction	a.	b.	c.	d.	Residue.
Temperature	56.40—56.45°	56.46°	59.16°	61.97°	—
Weight of fraction	6.10	20.3	6.4	19.76	16.6
Δ per cent.	174	2882	2.1	10.6	—

$$\Delta \text{ per cent.} = \frac{\text{Weight of fraction} \times 100}{\text{Weight of mixture taken} \times \text{interval of temperature}}$$

Δ per cent. is large when a substance is distilling at almost constant temperature, and is small when there is a rapid rise of temperature during the collection of a fraction. Its value for fraction (a) is not important as the thermometer takes time to reach the true temperature. The first few c.c. are therefore distilled slowly; afterwards, the constant rate of one drop per second is maintained. The large value of Δ per cent. for fraction (b) shows that a definite azeotropic mixture is distilling.

The temperature of this distillate was 21°; its weight was 20.3 grams, and 0.95 gram of aqueous layer separated out. This aqueous layer was saturated with ester. From the data given in the previous communication we see that it contained 7.8 per cent. of ethyl acetate. Therefore, the weight of water was 0.88 gram.

The weight of the ester layer was 19.25 grams, and from the solubility results we know it contained 3.04 per cent., or 0.60 gram, of water. The total weight of water in the 20.30 grams of azeotropic mixture was therefore 1.48 grams, or 7.30 per cent.

The composition of the azeotropic mixture may also be estimated by Young and Fortey's method (T., 1902, **81**, 752). This method assumes that the total weight of the azeotropic mixture is equal to the weight of the distillate which comes over below the middle temperature between its boiling point and the boiling point of the pure substance from which it is separating. The boiling point of the azeotropic mixture at 446.2 mm. is 56.44°, and that of the residue (ethyl acetate) 61.87°. The middle temperature is therefore 59.16°. The weight of distillate below this temperature was 32.8 grams. The total "loss" during the distillation was 1.28 grams, and the proportion of this below the middle point was taken to be 0.7 gram. Therefore the total weight of the azeotropic mixture was 33.5 grams, and this contained the whole of the water (2.51 grams), so that the percentage of water was 7.50.

B. Water in Excess.

Ethyl acetate, 46.93 grams; water, 51.72 grams.

Fraction.....	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	Residue.
Temperature	56.40—56.44°	56.46°	71.09°	85.75°	—
Weight of fraction	8.82	39.06	2.05	13.60	32.0
Δ per cent.	224	1982	0.14	0.95	—

Δ per cent. was again large for fraction (*b*), showing that there was a good separation of the azeotropic mixture from the excess of water. Fraction (*d*) consisted of water containing a small quantity of the ester. The rise in temperature from 71.09° to 85.75° was very rapid, so that practically the whole of the fraction distilled at the latter temperature. An aqueous layer, at a temperature of 19.5° and weighing 1.85 grams, separated from fraction (*b*). This layer contained 7.9 per cent., or 0.14 gram, of ester, so that the water present weighed 1.71 grams. The ester layer weighed 37.21 grams, and contained 2.98 per cent., or 1.11 grams, of water. The total weight of water in the 39.06 grams of azeotropic mixture was 2.82 grams, or 7.21 per cent.

An analysis by Young and Fortey's method was also carried out. The azeotropic mixture boils at 56.44°, and water at 85.75°; therefore the middle temperature was 71.09°. The total loss during the distillation was 3.13 grams. The wet column was weighed, then dried, and weighed again. The weight of water clinging to the column was thus found to be 2.50 grams; therefore the real loss by evaporation during the distillation of the azeotropic mixture was

0.63 gram. The weight of distillate below the middle point was 49.93 grams, so that the weight of the azeotropic mixture was 50.56 grams. This contained the whole of the ester (46.93 grams). The water content was therefore 3.63 grams, or 7.18 per cent.

C. The total distillates below the middle temperatures were mixed and redistilled. A large portion distilled at 56.44° . This is therefore the true boiling point of the azeotropic mixture at 446.2 mm. pressure. The weight of the distillate was 46.41 grams. The aqueous layer which separated out at 18° weighed 2.21 grams. This contained 8.05 per cent. of ester or 2.03 grams of water. The ester layer weighed 44.40 grams, and contained 2.91 per cent., or 1.31 grams, of water. The total weight of water was 3.34 grams, so that the azeotropic mixture contained 7.20 per cent. of water. Five values for the percentage of water were thus obtained, giving a mean value for the percentage of water in the azeotropic mixture of ethyl acetate and water at 446.2 mm. pressure of 7.28.

The azeotropic mixture was collected in a receiver, sketched in Fig. 2. The aqueous layer separated out in the narrow tube A, which was carefully graduated.

FIG. 2.



The above process was carried out at nine different pressures; single distillations were also performed at eleven other pressures. The experimental results are given in table I. The construction of this table involved the carrying out of about fifty fractionations. The percentages of water, the boiling points of the azeotropic mixtures, and the differences between these boiling points and the boiling points of ethyl acetate lie on the smooth curves given in Fig. 3.

II.—The Azeotropic Mixture at 25 mm. Pressure.

Ordinary fractional distillations could not be carried out at this pressure, as the boiling point of the azeotropic mixture was below zero. The apparatus used in determining the vapour pressures of ethyl acetate and alcohol at low temperatures (Wade and Merri-
man, T., 1912, 101, 2441; Merriman, this vol., p. 628) was adopted for the work described in this section. A mixture of ethyl acetate and water of known composition was placed in the apparatus, and the pressure kept at the constant value of 25 mm. while the mixture steadily boiled. When about a third of the mixture had boiled away, the residue was weighed and its decomposition determined. Knowing the weight and composition of the mixture started with and of the residue, the composition of the distillate

could be readily calculated. The process was repeated until a mixture was obtained, which still had the same composition after half of it had evaporated, and the boiling point had remained constant throughout the evaporation. The desired result was obtained after six experiments, two of which are detailed below.

A. A mixture with a "cloudy point" of 46° was taken; the percentage of water was 4.22. The weight of the mixture was 56.03 grams, and the boiling point remained constant at -1.90° , whilst 26.78 grams evaporated. The cloudy point of the residue was 51° ; it therefore contained 4.50 per cent. of water, so that the distillate contained 3.83 per cent.

B. A mixture weighing 62.43 grams, with a cloudy point of 33.5° , was taken; the percentage of water was thus 3.60. The boiling point remained constant at -1.90° , while 32 grams evaporated, and the cloudy point of the residue remained unchanged at 33.5° , showing that no fractionation had occurred. Therefore, at 25 mm. pressure, the azeotropic mixture of ethyl acetate and water boiled at -1.90° and contained 3.60 per cent. of water.

TABLE I.

Experimental Results.

(a) Pressure in mm.	(b) Number of values obtained.	(c) Percentage of water in azeotropic mixture (mean).	(d) Boiling point of azeotropic mixture.	(e) Boiling point of ethyl acetate.	(f) Difference between the two boiling points.
25.0	1	3.60	-1.90°	0.61°	2.51°
50.0	1	3.96	+10.05	12.75	2.70
78.5	2	4.30	18.45	21.47	2.99
82.2	1	4.40	19.38	22.38	3.00
150.0	1	5.39	31.35	34.93	3.58
176.0	5	5.60	34.82	38.61	3.79
250.0	1	6.28	42.55	46.87	4.32
329.8	5	6.85	49.06	53.84	4.78
420.0	1	7.24	54.94	60.27	5.33
446.2	5	7.28	56.44	61.87	5.43
606.0	1	7.91	64.33	70.50	6.17
613.8	5	7.98	64.60	70.82	6.22
745.0	1	8.35	69.83	76.55	6.72
760.0	5	8.47	70.38	77.15	6.77
875.0	1	8.76	74.38	81.51	7.13
903.5	5	8.86	75.23	82.45	7.22
984.3	5	9.01	77.66	85.19	7.53
1177.9	5	9.46	82.95	90.99	8.04
1415.0	1	9.90	88.49	97.16	8.67
1441.3	5	9.94	89.08	97.80	8.72

The values at even pressures given in table II were deduced with the aid of the smoothed curves and the first and second difference curves.

TABLE II.

Smoothed Values at Even Pressures.

Pressure in mm.	Composition of azeotropic mixture in percentage of water (c).	Rate of change of composition with the pressure dc/dp (per mm.).	Boiling point of azeotropic mixture (t).	dt/dp (per mm.).	Difference between boiling points of ethyl acetate and the azeotropic mixture.
25	3.60	0.0166	-1.89°	0.618°	2.50
50	4.00	0.0153	+10.01	0.368	2.74
75	4.36	0.0140	17.45	0.258	2.97
100	4.70	0.0129	23.03	0.202	3.19
200	5.79	0.0092	37.55	0.112	3.97
300	6.56	0.0064	46.81	0.0796	4.63
400	7.11	0.0048	53.77	0.0618	5.21
500	7.54	0.0040	59.26	0.0510	5.71
600	7.92	0.0035	64.06	0.0436	6.16
700	8.25	0.0031	68.16	0.0385	6.56
760	8.43	0.0029	70.37	0.0361	6.78
800	8.54	0.0027	71.81	0.0350	6.92
900	8.80	0.0025	75.14	0.0318	7.25
1000	9.04	0.0023	78.17	0.0290	7.56
1100	9.26	0.0022	80.95	0.0268	7.85
1200	9.47	0.0020	83.53	0.0248	8.12
1300	9.67	0.0019	85.93	0.0232	8.38
1400	9.86	0.0019	88.18	0.0218	8.62
1500	10.04	0.0018	90.30	0.0206	8.85

Discussion of Results.

The proportion of water in the azeotropic mixtures of ethyl acetate and water increases regularly with increase of pressure. The rate of increase becomes continuously slower as the pressure rises, but there is no indication of the percentage of water ever reaching a constant value. The first and second differences of the percentages of water lie on smooth curves which contain no breaks or sudden changes of curvature. There is therefore no evidence of the formation of definite hydrates.

A study of the mutual solubilities of ethyl acetate and water (preceding paper) shows that the azeotropic mixtures of ethyl acetate and water, at all pressures, form two layers right up to the boiling points of the mixtures. The vapour-pressure curve is therefore of type 4C at all temperatures. The vapour-pressure curves at three temperatures drawn from the data given in table III are given in Fig. 3.

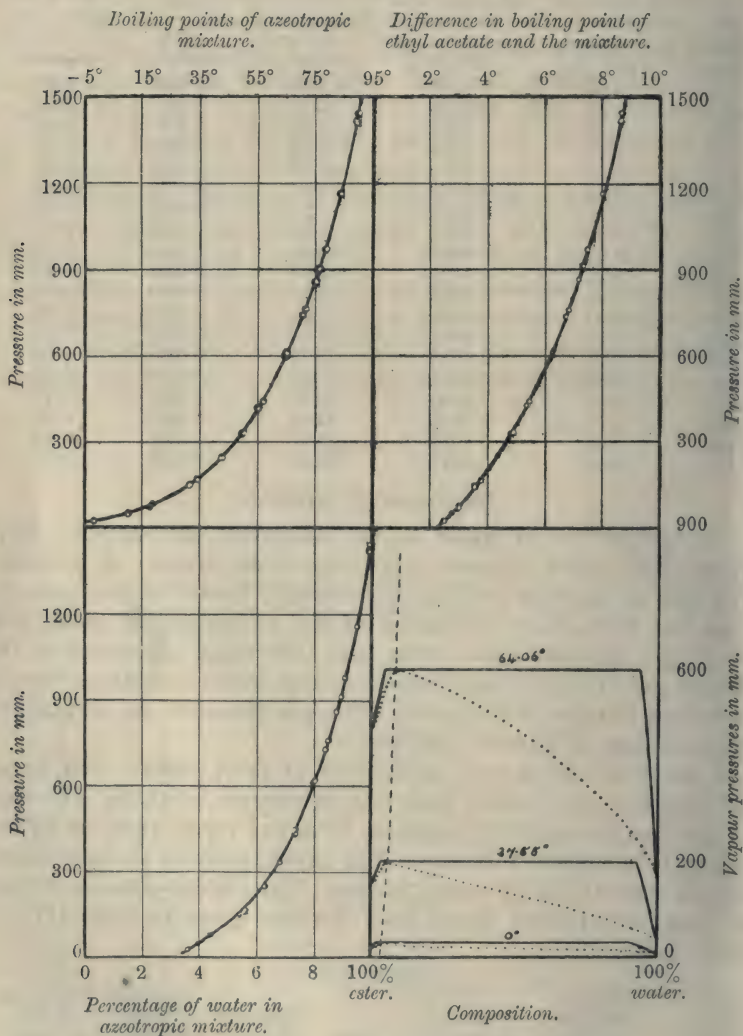
TABLE III.

Temperature.	Vapour pressure of azeotropic mixture. mm.	Vapour pressure of ethyl acetate. mm.	Vapour pressure of water. mm.	Percentage of water in the azeotropic mixture.	Percentage of water in ester saturated with water.	Percentage of ester in water saturated with ester.
0.0°	28.4	24.1	4.6	3.66	2.3	10.1
37.55	200.0	166.0	48.0	5.79	3.8	6.8
64.06	600.0	482.0	179.0	7.92	5.3	5.8

The dash-line represents the compositions of the azeotropic mixtures at different pressures.

Marshall (*loc. cit.*) proved that for miscible liquids the following

FIG. 3.



expression holds at a point of maximum or minimum vapour pressure:

$$\frac{p_1}{p_2} = \frac{x}{1-x},$$

where p_1 and p_2 are the partial pressures of the two substances, x is the molecular fraction of the first substance in the liquid and vapour, and $(1-x)$ is the molecular fraction of the second substance. This equation cannot, strictly speaking, be applied to the case of ethyl acetate and water, because there are two layers of different compositions in the distilling flask. The addition of one of the components merely alters the relative amounts of the two layers, which remain of the same compositions as before; so that the relative quantities of the ester and water may be varied, within wide limits, without changing the compositions of the liquid phases. The composition of the vapour phase is different from the composition of either of the liquid phases. It is only with miscible liquids that the compositions of the vapour and liquid phases at a point of maximum or minimum vapour pressure are the same. If we apply Marshall's expression to the vapour phase in the case of ethyl acetate and water, very interesting results are obtained. The following table was constructed in this way.

TABLE IV.

(a) Pressure in mm.	(b) Boiling point of azeotropic mixture.	(c) Percentage of water in the vapour phase.	(d) Molecular fraction of water (x).	(e) Partial pressure of water (p_1). mm.	(f) Partial pressure of ethyl acetate (p_2). mm.	(g) Vapour pressure of pure water at given temper- ature. mm.	(h) Vapour pressure of ethyl acetate at given temper- ature. mm.
1500.0	90.30°	10.04	0.354	531.0	969.0	531.6	1152.0
1000.0	78.17	9.04	0.328	328.0	672.0	329.3	785.0
760.0	70.37	8.43	0.310	236.0	524.0	237.1	603.0
600.0	64.06	7.92	0.296	177.7	422.3	179.0	482.0
200.0	37.55	5.79	0.231	46.2	153.8	48.0	166.0
28.4	0.0	3.66	0.157	4.46	23.94	4.6	24.1

It will be seen that the calculated partial pressure of water given in column (e) is in every case very nearly equal to the vapour pressure of pure water (column g) at the temperature of the experiment. The agreement throughout is remarkable, and probably is of definite physical significance.

The calculated partial pressure of the ethyl acetate (column f) is always appreciably less than the vapour pressure of pure ethyl acetate (column h) at the same temperature.

Duhem ("Mécanique Chimique," 1899, 4, 204) formulated a law relating to the vapour pressures of saturated solutions of partly miscible liquids, known as the "Duhem-Regnault" law. This law states that in the case of partly miscible liquids the total pressure of the heterogeneous mixture is equal to the vapour pressure of the more volatile constituent in the pure condition. This law is tested for the case of ethyl acetate and water in the following table:

TABLE V.

Temperature.	Vapour pressure of azeotropic mixture. mm.	Vapour pressure of ethyl acetate. mm.
90·30°	1500	1152
78·17	1000	785
70·37	760	603
64·06	600	482
37·55	200	166
0·0	28·4	24·1

It will be seen that the Duhem-Regnault law is far from true for the case under discussion. The formulation of such an inaccurate law was rendered possible by the lack of knowledge of the effect of change of pressure on the boiling points of azeotropic mixtures. It will be seen from table II that as the pressure is reduced, the boiling point of the azeotropic mixture becomes nearer and nearer to that of the more volatile of the components (ethyl acetate). It at once follows that the vapour pressure of the azeotropic mixture becomes continuously nearer to that of the ethyl acetate, as shown in table V. In the case of ethyl acetate and water, the difference between the boiling points of the ester and the azeotropic mixture is appreciable, even at the lowest pressures, so the Duhem-Regnault law is not true for these mixtures at any temperature.

The law was based on Regnault's work on the vapour pressures of ether saturated with water. Examining this mixture in the same way as the ethyl acetate and water mixture, we find that ether forms an azeotropic mixture with water which boils only 0·34° below the boiling point of ether (Wade and Finnemore, T., 1909, 95, 1849). The present work and the previous work with ethyl alcohol and water (Merriman, this vol., p. 635) on the effect of change of pressure on the boiling points of azeotropic mixtures shows that as the pressure is lowered the boiling points of the azeotropic mixture and of the volatile component continually approach each other. From this it is probable that at low pressures the boiling point of the azeotropic mixture of ether and water will be very close to the boiling points of ether, so that the two vapour pressures at a given low temperature will also be very near each other; Regnault's results on the vapour pressures of mixtures of ether and water at low temperatures are thus easily explained. His results at higher temperatures also followed the Duhem-Regnault law, so they must be quite inaccurate, as the difference in boiling point of 0·34° would correspond with a difference in vapour pressure of about 9 mm. The difficulty of preparing pure ether (Wade and Finnemore, *loc. cit.*) affords an explanation of Regnault's results.

These considerations, combined with a study of the curves of types 4A, 4B, 4C in Fig. 1, will clearly show that the "Duhem-Regnault law" is approximately true for only a few exceptional cases, and the "law" could now conveniently be discarded.

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CXCV.—*The Azeotropic Mixtures of Ethyl Acetate, Ethyl Alcohol, and Water at Pressures Above and Below the Atmospheric Pressure. Part II.*

By RICHARD WILLIAM MERRIMAN.

I.—*The Azeotropic Mixtures of Ethyl Acetate and Ethyl Alcohol.*

THE two methods used in the work described in Part I. are not applicable to the study of the azeotropic mixtures of ethyl acetate and ethyl alcohol.

The Young and Fortey method of analysis cannot be applied, because the separation of the azeotropic mixture from excess of the ester or alcohol is very imperfect. There is no sudden rise in temperature from the boiling point of the azeotropic mixture to that of the liquid present in excess, as there is in the case of ethyl acetate and water. The Young and Fortey method only gives concordant results when fractionation brings about a good separation of the liquids.

The second method depending on the separation of the two components into layers cannot be used because ethyl acetate and ethyl alcohol are miscible in all proportions.

The method adopted for the present work was exactly the same as the one used in the case of ethyl alcohol and water (Wade and Merriman, T., 1911, 99, 999).

A preliminary series of fractionations of mixtures of ethyl acetate and ethyl alcohol at wide intervals of pressure is carried out. In this way the curve showing the relations between the percentage of alcohol in the azeotropic mixtures and the pressure can be drawn with approximate accuracy. The approximate composition of the azeotropic mixture at any pressure can be read from this curve. Three careful fractionations are then carried out at each particular pressure.

In the first case, a mixture of ester and alcohol is made up, which contains rather less alcohol than the azeotropic mixture. The

manostat is set to the desired pressure, and the mixture carefully fractionated. The densities of an early and a late fraction are determined, and the compositions are read from a table of densities. The percentage of alcohol decreases during the fractionation, showing that the first fraction contains less than the correct quantity of alcohol. The gradient of separation is calculated by dividing the decrement in the percentage of alcohol in the two fractions by the relative increase in the total amount distilled; for instance, supposing the first fraction examined contained 35 per cent. of alcohol, and at the middle point of the fraction 0.20 of the whole of the mixture had distilled; and the next fraction dealt with contained 34.85 per cent. of alcohol, and at the middle point 0.80 of the whole mixture had distilled, the gradient of separation would be:

$$\frac{34.85 - 35.00}{0.80 - 0.20} = -\frac{0.15}{0.60} = -0.25.$$

The minus sign means that the percentage of alcohol is decreasing.

In the second case, a mixture of ester and alcohol is taken, which contains more alcohol than the azeotropic mixture. The mixture is fractionated, and two fractions are examined as before. The percentage of alcohol increases during the fractionation, showing that the first fraction contains more than the right amount of alcohol. The gradient of separation is calculated. Again taking a hypothetical example, the first fraction contained 35.30 per cent. of alcohol, and 0.25 of the whole mixture had distilled at the middle point of this fraction; the second fraction contained 35.45 per cent. of alcohol, and the stage of the distillation was 0.75. The gradient of separation was therefore:

$$\frac{35.45 - 35.30}{0.75 - 0.25} = \frac{0.15}{0.50} = 0.30.$$

It is clear that the correct quantity of alcohol in the azeotropic mixture would be between 35.00 and 35.30 per cent., and would be represented with sufficient accuracy by the expression:

$$\begin{aligned} & 35.00 + \frac{0.25 (35.30 - 35.00)}{0.25 + 0.30} \\ &= 35.00 + \frac{0.25 \times 0.30}{0.55} \\ &= 35.00 + 0.13 = 35.13 \text{ per cent.} \end{aligned}$$

In the third case a mixture containing the above percentage of alcohol is distilled, and the boiling point and composition should remain constant throughout the distillation.

II.—The above process was carried out at nine different pressures,

It is unnecessary to give the full details at every pressure, but the experiments at 948 mm. are given because of the interest lying in the fact that the vapour-pressure curves of ethyl alcohol and ethyl acetate cross at this pressure (Merriman, this vol., p. 635).

A. Alcohol in Slight Excess.

Pressure = 948 mm.
 Weight of mixture taken = 99.60 grams.
 Density of mixture = 0.88025 0°/0°.
 Percentage of alcohol = 33.55.

	a.	b.	c.	Residue.
Temperature	78.13°	78.15°	78.17°	= 32 grams
Weight of fraction ...	8.71 grams	29.35	28.76	Loss = 0.86 gram
Stage of distillation ...	0.044	0.234	0.526	—
Density of fraction ...	—	0.88047 0°/0°	0.88039 0°/0°	0.88006 0°/0°
Per cent. of alcohol ...	—	33.37	33.44	33.71

$$\text{Gradient of separation} = \frac{33.44 - 33.37}{0.526 - 0.234} = \frac{0.07}{0.292} = 0.24.$$

B. Ester in Slight Excess.

Weight of mixture taken = 98.75 grams.
 Density of mixture = 0.88093 0°/0°.
 Percentage of alcohol = 33.00.

	a.	b.	c.	Residue.
Temperature	78.14°	78.15°	78.17°	= 28.90 grams
Weight of fraction ...	10.44 grams	31.06	27.65	Loss = 0.70 gram
Stage of distillation...	0.053	0.263	0.56	—
Density of fraction ...	—	0.88075 0°/0°	0.88087 0°/0°	0.88118 0°/0°
Per cent. of alcohol ...	—	33.15	33.06	32.80

$$\text{Gradient of separation} = \frac{33.06 - 33.15}{0.56 - 0.263} = -\frac{0.09}{0.297} = -0.30.$$

The percentage of alcohol in the azeotropic mixture =

$$33.15 + \frac{0.30 \times (33.37 - 33.15)}{0.30 + 0.24} = 33.15 + 0.12 = 33.27 \text{ per cent.}$$

C. Ester and Alcohol evenly Balanced.

Density of mixture taken = 0.88063 0°/0°.
 Percentage of alcohol = 33.24.

The mixture distilled without change of composition at a temperature of 78.13°.

Therefore the azeotropic mixture of ethyl acetate and ethyl alcohol at 948 mm. pressure contained 33.27 per cent. of alcohol, and boiled at 78.13°. It is interesting to observe that two liquids which boil at the same temperature can be partly separated by fractional distillation. At the pressure of 948 mm. both the alcohol and ester boil at 84.01°. If we distilled a mixture of equal weights

of ethyl alcohol and ethyl acetate at this pressure, through a very efficient fractionating column, the azeotropic mixture would distil at a temperature of 78.13° , whilst the last fraction would be pure alcohol boiling at 84.01° .

The experimental results at all the pressures are given in table I.

III.—*The Azeotropic Mixture of Ethyl Acetate and Ethyl Alcohol at 25 mm. Pressure.*

The evaporation method previously described was used at this pressure. Various mixtures were allowed to boil away at constant pressure until one was found which showed no change in composition during the evaporation, and boiled at a constant temperature throughout the experiment.

Four of the experiments are detailed in the following scheme:

	1st Expt.	2nd Expt.	3rd Expt.	4th Expt.
Weight of mixture taken...	59.10	45.50	61.28	55.54
Density of mixture $0^{\circ}/0^{\circ}$...	0.90424	0.90631	0.90792	0.90684
Percentage of alcohol	14.80	13.25	12.05	12.85
Rise in temperature during experiment.....	-1.30° to -1.25°	-1.37° to -1.30°	-1.37° to -1.27°	Constant at -1.37°
Weight of residue	39.34	37.50	37.39	30.25
Density of residue $0^{\circ}/0^{\circ}$...	0.90366	0.90626	0.90824	0.90683
Percentage of alcohol	15.23	13.28	11.81	12.86
\therefore Percentage of alcohol in distillate.....	13.95	13.11	12.42	12.84

Therefore the azeotropic mixture of ethyl acetate and ethyl alcohol at 25 mm. pressure boiled at -1.37° , and contained 12.85 per cent. of alcohol.

TABLE I.

Experimental Results.

(a) Pressure in mm.	(b) Per cent. of alcohol in azeotropic mixture.	(c) Boiling point of azeotropic mixture.	(d) Boiling point of ethyl acetate.	(e) Difference between the two boiling points.
25.0	12.85	-1.37°	0.61°	1.98°
77.4	15.95	18.71	21.01	2.30
117.2	17.60	27.02	29.60	2.58
219.9	21.21	40.50	43.73	3.23
423.0	25.79	56.31	60.46	4.15
578.2	28.41	64.43	69.16	4.73
760.0	30.93	71.81	77.15	5.34
948.0	33.27	78.13	84.01	5.88
1121.0	35.22	83.05	89.42	6.37
1475.5	38.87	91.35	98.60	7.25

The values given in columns (b), (c), and (e) lie on smooth curves drawn in Fig. 1. These curves were smoothed by means of the first and second difference curves, and the values at even pressures given in table II were thus obtained.

TABLE II.

Pressure in mm. (<i>p</i>).	Percentage of alcohol in azeotropic mixture. (<i>c</i>).	dc/dp (per mm.).	Boiling point of azeotropic mixture. (<i>t</i>)	Difference between boiling points of ethyl acetate and the azeotropic mixture.	
				dl/dp (per mm.).	
25	12.81	0.0760	-1.39°	0.7000°	2.00°
50	14.49	0.0610	+10.58	0.3700	2.17
100	16.97	0.0430	23.72	0.2080	2.50
200	20.52	0.0306	38.42	0.1160	3.10
300	23.22	0.0240	47.83	0.0810	3.61
400	25.37	0.0195	54.92	0.0630	4.06
500	27.17	0.0168	60.62	0.0520	4.45
600	28.75	0.0150	65.40	0.0445	4.82
700	30.18	0.0137	69.57	0.0395	5.15
760	30.98	0.0130	71.81	0.0366	5.34
800	31.49	0.0126	73.27	0.0352	5.46
900	32.71	0.0119	76.63	0.0320	5.76
1000	33.86	0.0112	79.68	0.0291	6.05
1100	34.36	0.0108	82.48	0.0270	6.32
1200	36.03	0.0105	85.07	0.0250	6.58
1300	37.07	0.0102	87.48	0.0232	6.83
1400	38.08	0.0100	89.74	0.0218	7.06
1500	39.07	0.0098	91.86	0.0205	7.29

IV.—*Discussion of Results.*

The percentages of alcohol in the azeotropic mixture and the boiling points of the mixtures, when plotted against the pressure, lie on smooth curves. Although the vapour-pressure curves of ethyl acetate and ethyl alcohol cross at a pressure of 948 mm., there is no change of direction in the above curves at this pressure. The first and second difference curves are also smooth, showing neither breaks nor changes of direction. There is thus no indication of a binary compound of ethyl acetate and ethyl alcohol. Following the course of the previous cases investigated, the proportion of alcohol in the azeotropic mixture increases continuously with the pressure, and shows no signs of reaching a constant value. Marshall's formula, $p_1/p_2 = x/(1-x)$, should be strictly applicable to mixtures of ethyl alcohol and ethyl acetate, as they are miscible in all proportions. The results of the application of this formula are given in table III.

TABLE III.

Boiling point of the azeotropic mixture.	Pressure in mm.	Percentage of alcohol in liquid and vapour.	Molecular fraction of alcohol (<i>x</i>).	Partial pressure of the alcohol (<i>p</i> ₁).	Partial pressure of the ethyl acetate (<i>p</i> ₂).	Vapour pressure of pure alcohol at the given temperature.	Vapour pres- sure of pure ethyl acetate at the given temperature.
0.0°	27	12.94	0.221	6.0	21.0	12	24.1
38.42	200	20.52	0.331	66.2	133.8	124	175
60.62	500	27.17	0.417	208.5	291.5	362	425
71.81	760	30.98	0.462	351.0	409.0	585	634
79.68	1000	33.86	0.495	425.0	505.0	802	825
91.86	1500	39.07	0.554	831.0	669.0	1269	1208

In order to trace the effect of each liquid on the vapour pressure of the other liquid, the following table was constructed.

TABLE IV.

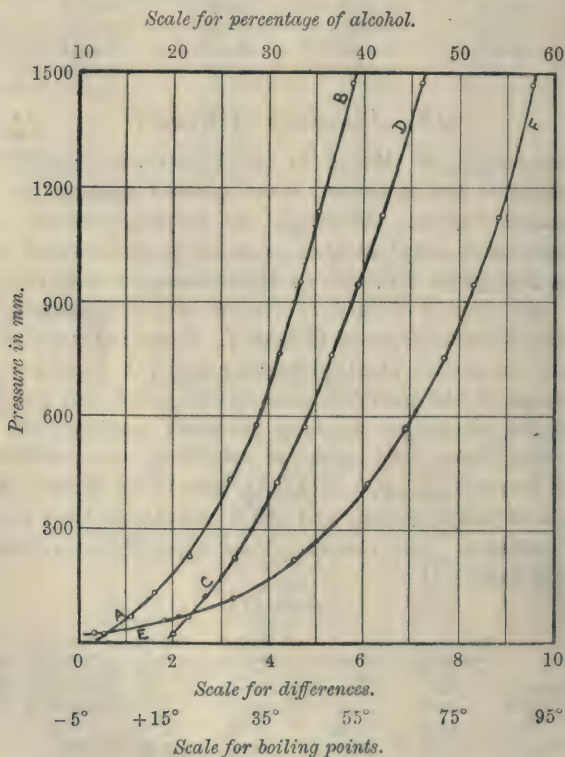
Temperature.	Partial pressure of	
	alcohol; vapour pressure of pure alcohol.	ester; vapour pressure of pure ester.
0.0°	0.50	0.87
38.42	0.535	0.765
60.62	0.576	0.685
71.81	0.600	0.645
79.68	0.617	0.612
91.86	0.656	0.554

FIG. 1.

AB = Percentage of alcohol in ester-alcohol mixture.

CD = Differences in boiling point between ethyl acetate and the mixture.

EF = Boiling points of the mixture.



It will be seen that at low temperatures the alcohol is affected more than the ester, as is to be expected, because the boiling point

of the azeotropic mixture is nearer to that of the ester than to the boiling point of the alcohol.

At high temperatures the ester is affected more than the alcohol, because the boiling point of the azeotropic mixture is now nearer to the boiling point of the alcohol than to the boiling point of the ester.

The effect on each liquid, however, does not become equal exactly at the pressure where the vapour-pressure curves cross each other, but at the rather higher pressure of 990 mm.

V.—*General Rule Relating to the Change of Composition of a Binary Azeotropic Mixture of Minimum Boiling Point with Change of Pressure.*

Although the vapour-pressure curves of ethyl alcohol and ethyl acetate cross at a pressure of 948 mm., yet the percentage of alcohol in the azeotropic mixture increases continuously with the pressure, and shows no break at the point of crossing of the vapour-pressure curves. The generally accepted rule (Merriman, this vol., p. 628) that the percentage of the liquid of lower boiling point decreases as the pressure increases, cannot therefore be valid for mixtures of ethyl acetate and ethyl alcohol at pressures above 948 mm.

It will be seen from Fig. 2(a) that the slope of the vapour-pressure curve of the ester is less steep than the alcohol curve, namely, dp/dt for ethyl acetate is less than for alcohol.

The general rule for the change of composition of an azeotropic mixture of minimum boiling point, which has been deduced from the present work, is that the percentage of the liquid for which dp/dt is smaller, increases as the pressure decreases. According to Bancroft's rule (preceding paper, p. 1790), liquids which have nearly equal values of dp/dt do not form azeotropic mixtures, as the vapour-pressure curves would not cross.

It will be seen from the curves in Fig. 2(b) that the new rule holds for the ethyl acetate–water mixtures, because dp/dt is less for the ester, and the percentage of ester increases as the pressure decreases (Part I., preceding paper).

The new rule was tested on other cases, in which the direction of change of composition with the pressure was known. The vapour-pressure curves in Fig. 2, drawn without regard to scale, are given in order to save a lengthy explanation of each case discussed below.

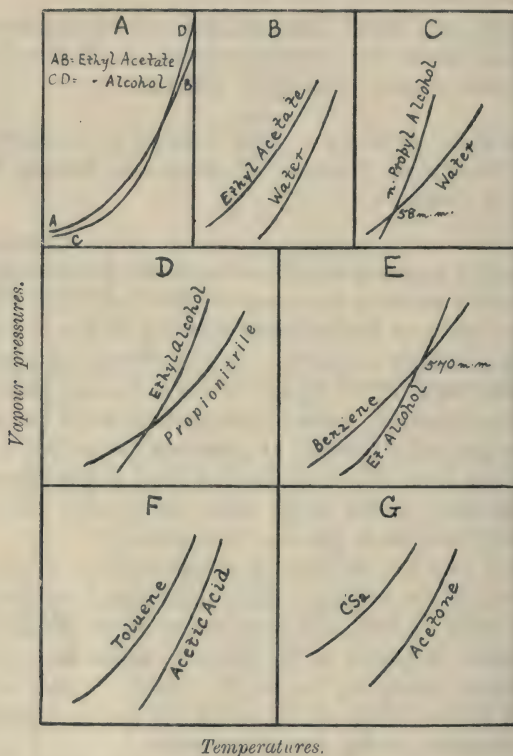
Case C. n-Propyl Alcohol and Water (Fig. 2 c).

dp/dt is smaller for the water. Young and Fortey (T., 1902, 81, 727) found, qualitatively, that the percentage of water in the azeotropic mixture increases as the pressure decreases.

Case D. Ethyl Alcohol and Propionitrile (Fig. 2 d).

dp/dt is smaller for the nitrile. Homfray (T., 1905, **87**, 1441) found that the percentage of nitrile increases as the pressure decreases.

FIG. 2.

*Case E. Ethyl Alcohol and Benzene (Fig. 2 e).*

dp/dt is smaller for benzene.

Thayer (*J. Physical. Chem.*, 1899, **3**, 36) found that at 66.5° the azeotropic mixture contained 33.5 per cent. of alcohol. Lehfeltdt (*Phil. Mag.*, 1898, [v], **46**, 42) found that at 50° the mixture contained 27.5 per cent. of alcohol, so that as the pressure decreases the percentage of benzene increases.

Case F. Toluene and Acetic Acid (Fig. 2 f).

dp/dt is smaller for toluene.

Ryland (*J. Amer. Chem. Soc.*, 1899, **22**, 384) found that at

760 mm. pressure the azeotropic mixture contained 70 per cent. of toluene. Zawidzki (*Zeitsch. physikal. Chem.* 1900. **35**, 459) found that at 336 mm. pressure it contained 78 per cent. of toluene and at 225 mm. pressure it contained 80 per cent.

Therefore the percentage of toluene increases as the pressure decreases.

Case G. Acetone and Carbon Disulphide (Fig. 2 g).

dp/dt is smaller for carbon disulphide.

Ryland (*loc. cit.*) found that at 760 mm. pressure the azeotropic mixture contained 66 per cent. of carbon disulphide. Zawidzki (*loc. cit.*) found that at 657 mm. pressure the azeotropic mixture contained 73 per cent. of carbon disulphide. Therefore the percentage of carbon disulphide increases as the pressure decreases.

The only exception to the general rule that the author has been able to find is the ethyl alcohol-water mixture (Wade and Merri-man, T., 1911, **99**, 997; Merriman, this vol., p. 628).

It was shown in the latter communication that dp/dt is smaller for the water; but the percentage of water in the azeotropic mixtures decreases as the pressure decreases. This case, however, is somewhat different from the other cases already considered, as the vapour-pressure curves of ethyl alcohol and water do not cut, although they continuously approach each other as the temperature decreases to the freezing point of water.

VI.—*The Ternary Azeotropic Mixtures of Ethyl Acetate, Ethyl Alcohol, and Water at Pressures Above and Below the Atmospheric Pressure.*

Discussion of the Experimental Method.

It is easily seen that should a ternary azeotropic mixture exist, its boiling point must be below those of any of the binary azeotropic mixtures. In the case of ethyl acetate, ethyl alcohol, and water, the boiling point of the ternary mixture, on the average, is within 0.15° of the boiling point of the ester-water binary mixture. The clean separation of the two mixtures by fractional distillation is therefore impossible. The only method of estimating the composition of a ternary azeotropic mixture is by the Young and Fortey method of analysis. The proportions of ethyl acetate, ethyl alcohol, and water must be chosen so that the second fraction is not the ester-water mixture, but either the ester-alcohol or alcohol water binary mixtures or any of the pure substances. The separation of the ternary mixture from either of the previously mentioned binary mixtures is by no means perfect, so that the

Young and Fortey method of analysis cannot give accurate results.

In the present work many distillations were carried out at each pressure. After each distillation the composition of the ternary mixture was estimated. These results varied to a relatively large extent. If, for instance, a large excess of alcohol was present in the original mixture in the distilling flask, the ternary mixture would contain too much alcohol. If a large excess of water was taken, so that two layers formed in the distilling flask, the ternary mixture merged into the ester-water mixture, so that the first fraction was cloudy, and deposited water. The Wade method of purifying ethyl acetate from ethyl alcohol (T., 1905, **87**, 165) by distilling from the water-bath with a large quantity of water depends on the instability of the ternary mixture. A large proportion of the alcohol is retained in the lower aqueous layer in the distilling flask.

After several fractionations, the probable composition of the ternary azeotropic mixture became known, and various mixtures were distilled until one was found which distilled at a constant temperature without change of density. The density of a ternary mixture of ethyl acetate, ethyl alcohol, and water is no guide as to its composition, as many different mixtures can be made up having the same density.

When a mixture of constant boiling point was obtained, attempts were made to estimate directly the amounts of alcohol and ester present in it. A known weight of it was saponified at 100° in a sealed tube by means of concentrated alcoholic sodium hydroxide. From the weight of alkali used, the weight of ester could be estimated. The results, however, of blank experiments were subject to an error of about 1 per cent., owing to the action of the sodium hydroxide on the glass.

Attempts to estimate both the alcohol and the ester, by saponifying with aqueous sodium hydroxide and distilling off the alcohol proved to be useless, owing to the small quantities that had to be used; thus the percentage of ester present in the ternary azeotropic mixture is known within 1 per cent., but the percentages of water and alcohol are somewhat doubtful, as they depend to a large extent on the Young and Fortey method of analysis. In the succeeding section some of the fractionations are described, illustrating the method of applying the Young and Fortey method of analysis to the study of a ternary mixture.

VII.—Pressure=1446·2 mm.

Boiling point of ethyl acetate	= 97·90°
„ „ ester-alcohol azeotropic mixture	= 90·75
„ „ alcohol-water „ „	= 95·25
„ „ water.....	= 119·04
„ „ ternary azeotropic mixture	= 88·96

Distillations 1, 2, 3, and 4 were carried out at this pressure.

Distillation 1. Alcohol and Water in Excess.

First stage: Ternary mixture	B. p. = 88·96°
Second „ : Alcohol-water	B. p. = 95·25
Third „ : Water	B. p. = 119·04
∴ Middle point between first and second stages, M_1	= 92·10
„ „ second and third stages, M_2	= 107·14

Ester (90·90 grams), alcohol (37·97 grams), water (49·83 grams) = 178·70 grams.

Fraction ..	a.	b.	c.	d.	e.	f.	Residue.
Temperature...	88·96—89·00°	89·03°	89·08°	89·35°	92·10°	107·14°	36·70 grams
Weight	31·70 grams	25·85	27·85	27·14	6·46	22·00	Loss = 1 gram
Δ per cent. ...	444	483	312	56·3	1·3	0·8	—
Density 15°/15°	0·9070	0·9043	0·9015	0·8969	—	0·8231	1·0

Young and Fortey Analysis.

Distillate between M_1 and M_2 = 22·00 grams of alcohol-water mixture. This contains 95·3 per cent., or 21·00 grams of alcohol, so that the ternary mixture contained 16·97 grams of alcohol.

The amount of ternary mixture is the weight of distillate below M_1 . This was 119·5 grams (119·0 + 0·5 “loss”), and contained ester (90·90 grams), alcohol (16·97), and water (11·63). Therefore the composition of the ternary mixture was: ester, 76·0; alcohol, 14·2; and water, 9·8 per cent.

As the second stage was moist alcohol, the percentage of alcohol given above must be too high.

Distillation 2. Excess of Alcohol and Ester.

First stage: Ternary mixture	B. p. = 88·96°
Second „ : Ester-alcohol binary mixture	B. p. = 90·75
Third „ : Ester	B. p. = 97·90
∴ Middle point between first and second stages, M_1	= 89·85
„ „ second and third stages, M_2	= 94·32

Ester, 87·63 grams; alcohol, 15·90 grams; water, 5·04 grams. Density = 0·8972.

Fraction ...	a.	b.	c.	d.	e.	Residue.
Temperature...	89·00—89·06°	89·15°	89·50°	89·85°	94·32°	25·67 gram
Weight	27·10 grams	26·15	12·90	3·85	12·30	Loss = 0·60 gram
Δ per cent. ...	416	263	34	10·1	2·5	—
Density	0·9022	0·8998	0·8923	—	0·8804	0·9068

The weight between M_1 and M_2 was 12·30 grams. This was ester-alcohol mixture, and therefore contained 4·80 grams of

alcohol, so that there was 11.10 grams of alcohol in the ternary mixture.

The weight below the middle point, M_1 , was 70.30 grams ($70.00 + 0.30$ "loss"). The alcohol present weighed 11.10 grams, and all the water (5.04 grams) must also have been included in this distillate; therefore, the ester content weighed 54.16 grams. Therefore, the composition of the azeotropic ternary mixture was: Ethyl acetate, 77.1; alcohol, 15.8; and water, 7.1 per cent.

The second stage was the ester-alcohol binary mixture, so that the above value for the percentage of alcohol must be appreciably too high. This is also indicated by the low density of the first fraction.

Distillation 3.

A mixture was made up which was likely to distil without change of composition:

Ethyl acetate.....	=	27.86 grams	=	77.6 per cent.
Alcohol	=	4.35 "	=	12.1 "
Water.....	=	3.69 "	=	10.3 "
Density	=	0.9095	15°/15°.	

The mixture distilled at a constant temperature of 88.96°, and the density of the distillate was 0.9094.

Distillation 4.

Ethyl acetate.....	=	70.73 grams	=	77.5 per cent.
Ethyl alcohol	=	12.10 "	=	12.1 "
Water.....	=	9.50 "	=	10.4 "
Density	=	0.9094	15°/15°.	

Fraction	a.	b.	Residue.
Temperature	88.94—88.96°	88.96°	38.30 grams.
Weight	23.73 grams	28.47	Loss=0.78 gram.
Density 15°/15°.....	0.9095	0.9094	0.9095

Estimation of Ester in Fraction (a).

The standard oxalic acid contained 15.8396 grams in 2 litres, and 1.2127 grams of the sodium hydroxide solution neutralised 40.04 c.c. of the oxalic acid.

1.6180 Grams of (a) and 5.2905 grams of the sodium hydroxide were heated for ten hours in a sealed tube at 100°. The excess of sodium hydroxide solution required 60.93 c.c. of oxalic acid for neutralisation, corresponding with 77.91 per cent. of ester. Therefore, the ternary azeotropic mixture of ethyl acetate, ethyl alcohol, and water at 1446.2 mm. pressure boiled at 88.96°, and had the approximate composition of: Ethyl acetate=77.6; ethyl alcohol=12.1; water=10.3 per cent.

The above process was repeated at different pressures, and the final results are given in table V.

VIII.—*The Ternary Azeotropic Mixture of Ethyl Acetate, Ethyl Alcohol, and Water at 25 mm. Pressure.*

The evaporation method was employed at this pressure.

Distillation 5.

Ethyl acetate	=	72.95 grams	=	92.54 per cent.
Ethyl alcohol	=	3.18 „	=	4.04 „
Water	=	2.69 „	=	3.42 „
Density	=	0.9142 9°/15°.		

The boiling point was -1.40° .

The residue weighed 39.5 grams; its density was $0.9140\ 9^{\circ}/15^{\circ}$, indicating the presence of a slight excess of alcohol in the mixture taken.

Distillation 6.

Ethyl acetate... ..	=	61.23 grams	=	91.1 per cent.
Ethyl alcohol	=	3.97 „	=	5.9 „
Water.....	=	2.00 „	=	3.0 „
Density	=	0.8976 $21^{\circ}/15^{\circ}$.		

The boiling point was -1.39° . The residue weighed 34.5 grams, and had a density of $0.8968\ 21^{\circ}/15^{\circ}$, indicating the presence of too much alcohol in the original mixture.

Distillation 7.

Ethyl acetate.....	=	64.73 grams	=	92.4 per cent.
Ethyl alcohol	=	2.79 „	=	4.0 „
Water.....	=	2.53 „	=	3.6 „
Density	=	0.9084 $15^{\circ}/15^{\circ}$.		

The boiling point was -1.41° . The residue weighed 33.6 grams, and had a density of $0.9078\ 15^{\circ}/15^{\circ}$, indicating the presence of too much alcohol in the original mixture.

Distillation 8.

Ethyl acetate	=	69.94 grams	=	90.5 per cent.
Ethyl alcohol	=	3.91 „	=	5.1 „
Water.....	=	3.40 „	=	4.4 „
Density	=	0.9089 $15^{\circ}/15^{\circ}$.		

The boiling point was -1.40° . The residue weighed 36.5 grams, and had a density of $0.9093\ 15^{\circ}/15^{\circ}$, indicating the presence of too much water in the original mixture.

Distillation 9.

Ethyl acetate	=	65.33 grams	=	92.00 per cent.
Ethyl alcohol	=	2.80 „	=	3.94 „
Water	=	2.88 „	=	4.06 „
Density	=	0.9072	15°/15°.	

The mixture boiled at -1.40° . The residue weighed 36.4 grams, and had a density of 0.9073 $15^{\circ}/15^{\circ}$.

Therefore the ternary azeotropic mixture at 25 mm. pressure boiled at -1.40° , and had the following approximate composition: Ethyl acetate, 92.0; ethyl alcohol, 4.0; water 4.0 per cent.

IX.—*Tables of Results.*

TABLE V.

Compositions of the Ternary Azeotropic Mixtures.

Pressure in mm.	Percentage of		
	ethyl acetate.	alcohol.	water.
25.0	92.0	4.0	4.0
178.5	88.4	5.6	6.0
503.6	84.8	7.2	8.0
760.0	82.6	8.4	9.0
1090.8	79.9	10.6	9.5
1446.2	77.6	12.1	10.3

The percentages of ethyl acetate, alcohol, and water are represented by the curves in Fig. 3.

The boiling points of the mixtures are given in table VI, and are compared with those of the ester-water binary mixtures. The two series of boiling points are very close together, becoming nearer as the pressure is decreased. The boiling point of the ternary mixture at even pressures can be readily calculated from the boiling points of the ester-water mixtures given in table II of Part I., by means of the differences given in table VII.

TABLE VI.

Pressure in mm.	Boiling point of		Difference between the two boiling points.
	the ternary mixture.	the ester-water mixture.	
25.0	-1.40°	-1.39°	0.01°
178.5	34.98	35.06	0.08
503.6	59.42	59.54	0.12
760.0	70.23	70.37	0.14
1090.8	80.51	80.71	0.20
1446.2	88.96	89.17	0.21

TABLE VII.

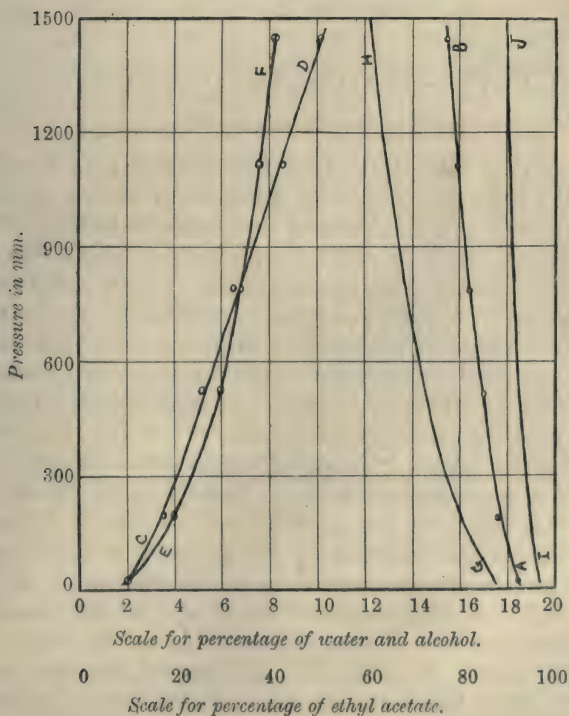
Pressure in mm.	Difference between boiling points of ternary mixture and ester-water mixture.
25	0·02°
200	0·07
400	0·11
600	0·13
760	0·15
1000	0·17
1200	0·19
1500	0·22

X.—*Discussion of Results.*

Two points of interest will be noticed. In the first place, the boiling points of the ternary mixtures are very close to those of the ester-water binary mixtures, so that at low temperatures the

FIG. 3.

AB = Percentage of ester in ternary mixture.
 CD = „ „ alcohol in ternary mixture.
 EF = „ „ water „ „ „
 GH = „ „ ester in ester-alcohol mixture.
 IJ = „ „ „ ester-water „ „



addition of alcohol to a mixture of ethyl acetate and water would have very little effect on the vapour pressure. In the second place, the percentage of water in the ternary mixture at any pressure is not greatly different from the percentage of water in the ester-water binary mixture (see Part I.), whilst the percentage of alcohol in the ternary mixture is much less than in the alcohol-ester binary mixture (see table II).

The percentages of ethyl acetate in the three azeotropic mixtures at different pressures are compared in the curves in Fig. 3. The curve showing the percentage of ester in the ternary mixture lies symmetrically between the other two curves.

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EAST LONDON COLLEGE.

GUY'S HOSPITAL.

CXCVI.—*The Dynamics of Bleaching.*

By SYDNEY HERBERT HIGGINS.

THE author (T., 1912, **101**, 222) drew attention to a relationship between the bleaching actions of solutions of sodium peroxide and of hypochlorites, and also between the rates at which these solutions give off oxygen when in contact with copper oxide. The contention was put forward from the results that copper oxide accelerates the production of oxygen gas from hypochlorites, which themselves give off pure oxygen (especially in sunlight), and that during the bleaching action the oxidisable matter present merely uses up this oxygen which is otherwise evolved. In this connexion it is interesting to note the observation of Lewis (T., 1912, **101**, 2371) that the evolution of oxygen from hypochlorite solutions under the action of light is a unimolecular action. Recently Bell (*Zeitsch. anorg. Chem.*, 1913, **82**, 145) has shown that the rate of decomposition of bleaching powder solution in the presence of small quantities of cobalt nitrate is proportional to the concentration of the components, and that the results obtained are in accordance with a unimolecular reaction. Using copper oxide as the catalytic agent, the present author (P., 1911, **27**, 314) stated that the production of oxygen from bleaching powder solution was a unimolecular

action, and later experiments with cobalt chloride as the catalyst, the oxygen evolved being carefully measured, have confirmed this view. Then Lemoine (*Bull. Soc. chim.*, 1913, [iv], 13, 5) has shown that the rate of decomposition of dilute solutions of hydrogen peroxide on heating is practically a unimolecular action.

These results serve to emphasise the analogies brought out by the author (*loc. cit.*) and to support the contention that bleaching is due to oxygen directly produced from hypochlorites. The author stated that this proposition could not be fully maintained without a careful study of the chemical changes taking place during the reactions described and by careful mathematical treatment. Careful tests have now been made on the action of bleaching powder solution on the colouring matters of vegetable fibres and on fibres dyed with indigo.

EXPERIMENTAL.

If, as above mentioned, hypochlorites in solution merely yield up their oxygen to the vegetable colouring matters during bleaching, the oxidation will be of the nature of a bimolecular reaction, and if the colouring matter be in large excess the action will be a bimolecular one of the first degree, or, according to van't Hoff, because there is a change in the concentration of only one molecular species, a unimolecular action. In order to obtain a large amount of colouring matter linen in the brown state was employed and was merely boiled with water under pressure before use. A very weak solution of bleaching powder was brought into contact with the linen cloth, and the velocity of the action was studied by titrating the bleaching powder solution at intervals with sodium thiosulphate after adding potassium iodide and hydrochloric acid. In actual experiments 51 sq. dcm. of linen cloth were placed in a 2-litre Jena-glass beaker containing 750 c.c. of water, and thoroughly soaked in it. Then 10 c.c. of bleaching powder solution (D 1.04) were added to 1 litre of water, and the mixture was poured on the linen. The whole was well stirred, and after an initial period of two minutes 10 c.c. of the weak bleaching liquor were titrated with *N*/500-sodium thiosulphate after adding potassium iodide and acidifying; starch solution was used as the indicator. At intervals of five minutes after stirring well, 10 c.c. were withdrawn to give the following results:

TABLE I.

t (5 mins.).	c.c. Thiosulphate.	c.c. Thiosulphate $-4.0 = a - x.$	$1/t \log a/a - x.$
0	19.7	15.7	—
1	13.1	9.1	0.2368
2	9.2	5.2	0.2399
3	7.2	3.2	0.2303
4	5.75	1.75	0.2382
5	5.0	1.0	0.2392
6	4.65	0.65	0.2305
7	4.35	0.35	0.2360
8	4.2	0.2	0.2410
24	4.05	—	—

With different conditions the following results were obtained:

TABLE II.

t (5 mins.).	c.c. Thiosulphate.	c.c. Thiosulphate $-4.0 = a - x.$	$1/t \log a/a - x.$
0	27.2	23.2	—
1	19.3	15.3	0.1838
2	14.2	10.2	0.1784
3	10.9	6.9	0.1755
4	8.65	4.65	0.1747
5	7.05	3.05	0.1762
6	5.9	1.9	0.1810
7	5.3	1.3	0.1788
8	4.9	0.9	0.1764
9	4.55	0.55	0.1808
10	4.45	0.45	0.1712
12	4.35	—	—
41	4.1	—	—

It was noticed in all cases that the bleaching powder solution did not bleach after a certain point had been reached, and at this point it was found that the bleaching liquor still liberated iodine from potassium iodide solution on adding acid, although it had no power of liberating the iodine in the absence of acid; at the commencement of the bleaching action the amount of iodine liberated from the iodide without acidifying was large, and became smaller and smaller until at the point mentioned the iodine liberated could hardly be discerned. It is also seen that the velocity of the bleaching action was directly related to the amount of iodine so liberated.

In order to arrive at the amount of the active bleaching substance one must subtract the residual non-active substance (which is probably calcium chlorate, since the bleaching powder solution used had remained for some time in a stoppered bottle) from the original titration, and this must be done in each case to give column 3, which is a measure of the active mass of the hypo-

chlorite causing the bleaching. The value of this final figure can usually be judged from the last titrations, but is best obtained by constructing a curve from the time and the amount of thiosulphate and finding where such curve runs parallel to the axis along which the time is marked. It is seen that the value of $1/t \log a/a-x$ is approximately constant, so that the action taking place during bleaching is a unimolecular one, that is, the oxygen is produced directly from the active hypochlorite present in solution.

Further tests were now made, using bleaching powder solution, to which (a) lime-water, and (b) a small quantity of hydrochloric acid had been added.

Rate of Bleaching of Bleaching Powder Solution to which Lime-water had been Added.

Instead of adding the bleaching powder solution mixed with 1 litre of water as in the previous experiment (table I), a mixture of 250 c.c. of lime-water and 750 c.c. of water was used in place of the water; the other conditions were as before. The results given in table III were obtained.

TABLE III.

t (5 mins.).	c.c. Thiosulphate.	c.c. Thiosulphate $-4.7=a-x$.	$1/t \log a/a-x$.
0	15.7	11.0	—
1	9.6	4.9	0.3511
2	6.8	2.1	0.3596
3	5.65	0.95	0.3545
4	5.1	0.4	0.3597
24	4.7	—	—

Rate of Bleaching of Bleaching Powder Solution to which a small amount of Hydrochloric Acid had been Added.

Instead of adding lime-water to the bleaching powder solution as in the previous experiment, 1 c.c. of *N*-hydrochloric acid was added to the litre of water, and the titrations were conducted as before. The results are shown in the following table:

TABLE IV.

t (5 mins.).	c.c. Thiosulphate.	c.c. Thiosulphate $-1.55=a-x$.	$1/t \log a/a-x$.
0	8.2	6.65	—
1	3.15	1.6	0.6187
2	1.95	0.4	0.6105
3	1.65	0.1	0.6110
4	1.6	0.05	—
5	1.55	—	—

Tables III and IV show that for bleaching powder solution with the additions given, $1/t \log a/a-x$ is approximately constant.

It was found impossible to obtain comparable figures for the three actions given in tables I, III, and IV because of the difficulty of obtaining even an approximately initial titration, but in the three experiments given these conditions were aimed at. An initial period of two minutes was allowed because (1) it is usual in studying such actions to allow such a period, and (2) the author has shown (P., 1912, **28**, 130; *J. Soc. Chem. Ind.*, 1913, **32**, 350) the possibility of chlorination taking place during this initial period.

Having performed the above experiments on the bleaching of the colouring matter of unbleached linen, further experiments were now made on the bleaching of indigo.

The Rate of Bleaching of Indigo by Bleaching Powder Solution.

Many trials were made before obtaining a suitable method of carrying out this test. Finally, it was decided to use the indigo dyestuff developed on a bleached cotton ground. The dyed cloth was used in precisely the same manner as the unbleached linen of the previous experiments, for in this way it was found that a large amount of the dyestuff could be presented to the action of the bleaching powder solution. Mention has been made above of the interference of the calcium chlorate in the titrations with thio-sulphate, so that an attempt was made to use Penot's alkaline arsenite method, which is not affected by the presence of chlorate, to estimate the hypochlorite present in solution. It was found, however, that this method was not as accurate for the present purpose as the one previously used. In order, however, to reduce the amount of chlorate to a minimum, freshly prepared bleaching powder solution was used. About 2.5 sq. metres of indigo-dyed cloth were boiled with water, dried, and immersed in 1 litre of water. Then 10 c.c. of bleaching powder solution were added to 1 litre of water, and the solution was poured on the dyed cloth. After stirring well for two minutes 10 c.c. of the liquor were titrated with *N*/500-sodium thiosulphate after adding potassium iodide and acidifying. At the intervals stated, further titrations were made to give the following results:

TABLE V.

<i>t</i> (5 mins.).	c.c. Thiosulphate.	c.c. Thiosulphate - 0.2 = $a - x$.	$1/t \log a/a \cdot x$.
0	26.0	25.8	—
1	17.5	17.3	0.1736
2	11.95	11.75	0.1708
3	8.0	7.8	0.1731
4	5.4	5.2	0.1738
5	3.55	3.35	0.1773
6	2.4	2.2	0.1778
18	0.2	—	—

Again it is noticed that the value of $1/t \log a/a-x$ is approximately constant, showing that the action of the hypochlorite on the indigo is a case of direct oxidation. It is also seen that in this experiment the amount of chlorate present in solution was very small.

LUNCARTY BLEACHFIELD,
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CXCVII.—*The Constitution of Aconitine.*

By OSCAR LISLE BRADY.

THERE has been considerable controversy over the empirical formula of aconitine, but that proposed by Freund and Beck (*Ber.*, 1894, **27**, 433) is now most generally accepted, namely, $C_{34}H_{47}O_{11}N$, although Schulze (*Apoth. Zeit.*, 1904, **18**, 783; 1905, **20**, 368) has recently proposed $C_{34}H_{45}O_{11}N$. There seems, however, no reason at present for departing from the formula of Freund and Beck, at least for aconitine of German origin; Dunstan (*T.*, 1905, **87**, 1653), however, maintains that the alkaloid from English sources has a different composition. The aconitine used in this investigation was procured in Germany, and corresponds in properties with the substance described by Freund and Beck; consequently the formula suggested by these authors is used throughout this paper.

Aconitine has been shown to possess four methoxyl groups, three hydroxyl groups, one *N*-methyl, one acetyl, and one benzoyl group, but of the constitution of the rest of the molecule little is known, although Ehrenberg and Purfürst (*J. pr. Chem.*, 1892, [ii], **45**, 605), by the distillation of aconine (the product of the hydrolysis of aconitine) with barium hydroxide, obtained what they believed to be quinoline or tetrahydroquinoline, indicating that aconitine belonged to the quinoline group of alkaloids. Carr (*T.*, 1912, **101**, 2241) has described a compound, to which he has given the name oxonitin, obtained by the decomposition of aconitine permanganate with dilute sulphuric acid at 40°. The present author (compare *P.*, 1912, **28**, 289) obtained this compound independently, in small yield, by warming to 80° a solution of aconitine in excess of dilute sulphuric acid with potassium permanganate. When aconitine itself is acted on by a neutral solution of potassium permanganate there is obtained a compound very similar to oxonitin, and on account of its general resemblance to that compound (particularly with regard to their melting points) it was at first regarded

by the author as identical with oxonitin. As considerably better yields of this compound were obtained it was employed in the greater portion of the author's earlier work, and the analytical figures published (*loc. cit.*), with the exception of the percentages of carbon and hydrogen, were obtained from this substance. It now appears, however, that the compound obtained by the oxidation of aconitine with neutral permanganate is not identical with oxonitin, but contains a larger percentage of carbon, as can be seen from the following table of analytical results:

	Mean of figures given by Carr (<i>loc. cit.</i>).	Preparation of oxonitin by author using Carr's method.	Author's original preparation of oxonitin in acid solution.	Oxidation with neutral permanganate crystallised from methyl alcohol and chloroform.	Last substance after a further crystallisation.
C	59.3	59.6	59.5	60.7	60.6
H	6.5	6.3	6.4	6.5	6.7
N	3.2	—	—	3.2	—
OMe ...	19.3	—	—	18.2	—

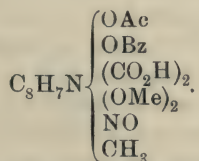
This new compound has been assigned the formula $C_{24}H_{29}O_9N$. It still retains the acetyl and benzoyl groups of aconitine; it is insoluble in most organic solvents, but dissolves more readily in chloroform than does oxonitin; it is also soluble in concentrated hydrochloric acid, being precipitated on dilution. When placed in the bath at 250° it melts and decomposes at 274° , and does not appreciably depress the melting point of oxonitin. As, however, the melting points of both these compounds depend largely on the rate of heating and are attended with decomposition, in the opinion of the author no justifiable conclusion can be drawn from their mixed melting point. The compound is a neutral substance combining with neither acids or alkalis; its solution in concentrated hydrochloric acid gives no precipitate with platinic chloride, whilst phenylhydrazine, semicarbazide, and hydroxylamine are without action on it.

By the action of nitric acid on aconitine an orange-yellow, crystalline substance melting at 205° has been obtained, to which it is proposed to assign the formula $C_{22}H_{26}O_{11}N_2$. This compound is a carboxylic acid dissolving readily in alkalis, and forming an amorphous silver salt. On warming an alkaline solution a small quantity of dimethylamine is evolved, the liquid darkens in colour, and mineral acids no longer give a precipitate with the solution; alkaline permanganate apparently decomposes the compound completely, dimethylamine is evolved, and acetic and benzoic acids are the only substances recoverable from the mixture.

The compound contains two methoxyl groups, and gives Liebermann's characteristic nitroso-reaction; hydrolysis with alkalis

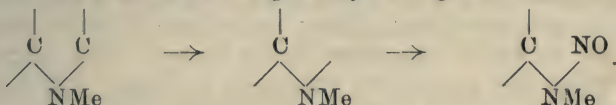
yields acetic and benzoic acids, so that the acetyl and benzoyl groups of aconitine are still present. Titration with *N*/10-alkali indicates the presence of two carboxyl groups, two equivalents of the base being neutralised.

In consideration of the above facts, and presuming that the *N*-methyl group of the aconitine has not been affected, the formula may be written:



This compound is of a comparatively simple nature, and the structure of the remaining part of the molecule should not be difficult to determine.

The position of the nitroso-group is at present uncertain, although it is possible that the compound is a nitrosoamine produced by the rupture of a nitrogenous ring and addition of the nitroso-group by the nitrous acid formed in quantity during the oxidation, thus:



The marked colour change, however (see p. 1825), observed during the preparation of this compound may be due to the formation of a nitrosoamine, and subsequent wandering of the nitroso-group into a nucleus.

It is noteworthy that the benzoyl group is not readily removed from this compound, and by boiling with 50 per cent. sulphuric acid for some hours under reflux and subsequent oxidation with hydrogen peroxide a compound melting at 269° has been obtained, which still contains the benzoyl group. This is being further investigated. The action of other oxidising agents on aconitine has also been tried, but so far without satisfactory results.

Alkaline ferricyanide, Caro's acid, hydrogen peroxide, or chromic acid in glacial acetic acid yielded nothing definite, whilst sodium hypobromite acted so vigorously, even in the cold, that the aconitine was completely decomposed.

When an aqueous solution of chromic acid is added to a solution of aconitine in dilute sulphuric acid a yellow precipitate of the dichromate, $\text{C}_{34}\text{H}_{47}\text{O}_{11}\text{N}, \text{H}_2\text{Cr}_2\text{O}_7$, is obtained, which on gentle warming in the solution forms a viscid mass. From the further investigation of this dichromate a small quantity of a crystalline substance resembling oxonitin has been obtained, but the amount

was too small for identification; beyond this, only benzoic and acetic acids have been separated.

EXPERIMENTAL.

Oxidation of Aconitine with Acid Permanganate.—The aconitine was dissolved in excess of dilute sulphuric acid, warmed to 80° , and potassium permanganate added from time to time until there was a slight effervescence. The crystalline precipitate was collected, suspended in water, and saturated with sulphur dioxide to remove traces of manganese oxides, collected, and recrystallised from a mixture of methyl alcohol and chloroform. This substance proved to be the oxonitin described by Carr (*loc. cit.*). (Found, $C=59.5$; $H=6.4$. $C_{23}H_{29}O_9N$ requires $C=59.6$; $H=6.2$ per cent.)

The yields obtained were very poor, being usually not more than 3 per cent. of the aconitine taken.

Oxidation of Aconitine with Neutral Permanganate.—Ten grams of aconitine were suspended in water, 2 grams of finely-powdered potassium permanganate added, and the mixture was gently warmed on a water-bath, when a vigorous action took place almost at once, acetaldehyde being evolved and a copious precipitate of brown oxides of manganese being formed. The liquid was filtered and the precipitate suspended in water, and the whole saturated with sulphur dioxide to dissolve the oxides of manganese. There remained suspended in the liquid a fine, crystalline substance, which was collected and recrystallised from chloroform and methyl alcohol:

0.1010 gave 0.2250 CO_2 and 0.0591 H_2O . $C=60.7$; $H=6.5$.

After again recrystallising:

0.1146 gave 0.2548 CO_2 and 0.0691 H_2O . $C=60.6$; $H=6.6$.

0.3580 „ 10 c.c. N_2 at 21° and 753 mm. $N=3.2$.

0.3266 „ 0.4508 AgI. $OMe=18.2$.

$C_{21}H_{29}O_9N$ requires $C=60.6$; $H=6.1$; $N=2.9$;

$3OMe=19.5$ per cent.

The molecular weight was determined by the ebullioscopic method in chloroform:

0.1530 in 19.7954 gave $E=0.065^{\circ}$. M.W.=431.

The substance melted at 272° if placed in the bath previously heated to 250° . The yield was not very satisfactory, being but 10—15 per cent. of the aconitine used.

Small quantities of a number of other substances have been obtained from the mother liquors of the acid and neutral oxidation of aconitine. One was insoluble and contained no nitrogen, and appeared to be an aldehyde; analysis of an impure specimen gave

C=63.2; H=5.9 per cent.; insufficient was, however, obtained for a more complete investigation. Another product was very soluble in water, and gave with bromine water a yellow precipitate of a bromo-derivative, which on collection dried to a sticky varnish, and was not further examined.

Action of Nitric Acid on Aconitine.—Fifteen grams of aconitine were dissolved in 100 c.c. of nitric acid (D 1.43) and heated on the water-bath. There was a copious evolution of brown nitrous gases, and at the end of an hour the mixture was poured into water. A copious, white precipitate was formed, which changed after a few minutes to a bright orange-yellow. The precipitate was collected, thoroughly washed with water, and crystallised from alcohol, when it formed an orange-yellow, crystalline powder, melting at 205°:

0.1002 gave 0.1966 CO₂ and 0.0517 H₂O. C=53.5; H=5.7.

0.1032 „ 0.2039 CO₂ „ 0.0516 H₂O. C=53.8; H=5.5.

0.1792 „ 8.8 c.c. N₂ at 20° and 773 mm. N=5.8.

0.1646 „ 0.1536 AgI. OMe=12.4.

C₂₂H₂₆O₁₁N₂ requires C=53.4; H=5.2; N=5.6;
2OMe=12.5 per cent.

The substance gave an abnormal depression of the freezing point in phenol, but 0.2722 in 8.569 of naphthalene gave $\Delta t = -0.445^\circ$. M.W.=494.

0.2700, dissolved in the cold in 50 c.c. of *N*/10-sodium hydroxide, required 39.7 c.c. *N*/10-sulphuric acid to neutralise the excess of sodium hydroxide, showing 10.3 c.c. used. Theory for 2CO₂H=10.8 c.c.

By adding silver nitrate to a solution of the substance in ammonia a yellow, amorphous precipitate of a silver salt was obtained, which deflagrated on heating:

0.1160 gave 0.0358 Ag. Ag=30.8.

C₂₂H₂₄O₁₁N₂Ag₂ requires Ag=30.5 per cent.

This substance when heated with alkaline permanganate evolved dimethylamine, but only acetic and benzoic acids could be recovered from the solution. The dimethylamine was identified by absorption in hydrochloric acid and preparation and analysis of its platinichloride. (Found, Pt=39.3. Calc., Pt=39.0 per cent.)

The compound dissolved readily in alkalis to form a yellow solution, which on warming darkened in colour, a small quantity of dimethylamine being evolved, and the substance could no longer be recovered unchanged from the liquid. After boiling for some time under reflux, acidifying, and distilling in a current of steam, benzoic and acetic acids were identified in the distillate, but ether extracted only a small quantity of a tarry matter from the solution.

Aconitine Dichromate.—An aqueous solution of chromic acid was added to a solution of aconitine in dilute sulphuric acid, and the yellow precipitate formed was rapidly filtered and dried in a vacuum. Analysis indicated that this substance was aconitine dichromate contaminated with inorganic matter.

Found: C=44·8; H=5·0; Cr₂O₃=18·7.

C₃₄H₄₇O₁₁N, H₂Cr₂O₇ requires C=47·2; H=5·6;
Cr₂O₃=17·6 per cent.

It was found impossible to purify this substance owing to its instability; on gentle warming it gives a dark viscid substance, from which no further results could be obtained.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for grants which have in part defrayed the expense of this research.

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CXCVIII.—*The Miscibility of Solids. Part II. The Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures.*

By ERNEST VANSTONE.

IN a previous paper (T., 1909, 95, 591), from a consideration of substances which form solid solutions in all proportions, it was suggested that the chief factors in the miscibility of solids are the shape and spacial domains of the molecules.

In order to study this subject further, a series of compounds having suitable melting points, and differing but little in constitution, was chosen for investigation by thermal analysis.

The following series of compounds was considered particularly adapted for the purpose. It will be observed that all the substances are of the type Ph α βPh.

Substance.	Formula.	M. p.
1. Benzylaniline	CH ₂ Ph·NHPh	36·0°
2. Phenyl benzyl ether	PhO·CH ₂ Ph	38·5
3. Phenylbenzylcarbinol	CH ₂ Ph·CHPh·OH	42·0
4. Benzylideneaniline	CHPh:NPh	49·5
5. Dibenzyl	CH ₂ Ph·CH ₂ Ph	52·5
6. Deoxybenzoin	COPh·CH ₂ Ph	56·0
7. Tolane	CPh ₃ CPh	62·5
8. Azobenzene	NPh:NPh	68·5

Substance.	Formula.	M. p.
9. Benzil	COPh•COPh	93·8
10. Thiobenzanilide	CSPh•NHPH	98·0
11. Stilbene	CHPh:CHPh	123·5
12. Hydrazobenzene	NHPH•NHPH	130·5
13. Benzoin	COPh•CHPh•OH	133·2
14. Hydrobenzoin	HO•CHPh•CHPh•OH	133·7
15. Benzanilide	COPh•NHPH	160·8

The above substances are arranged in order of their melting points, and the influence of constitution is clearly seen. The first and last members of the series show the opposite effects of the groups CH_2 and CO . The mean of these two melting points is the melting point of thiobenzanilide, $36 + 160\cdot8/2 = 98\cdot4^\circ$, or:

		Difference.
$\text{CH}_2\text{Ph}\cdot\text{NHPH}$	36·0°	62·0
$\text{CSPh}\cdot\text{NHPH}$	98·0	
$\text{COPh}\cdot\text{NHPH}$	160·8	62·8

62° is also the difference between the melting points of azobenzene and hydrazobenzene, and 61° between that of tolane and stilbene:

		Difference.
$\text{NHPH}\cdot\text{NHPH}$	130·5°	62
NPh:NPh	68·5	
CPh:CPh	62·5	61
CHPh:CHPh	123·5	

The difference between the melting points of stilbene and dibenzyl is, however, 71° . It will be noticed also that the melting point of benzil is almost the mean of the melting points of dibenzyl and hydrobenzoin:

		Difference.
$\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Ph}$	52·5°	41·3
$\text{COPh}\cdot\text{COPh}$	93·8	
$\text{HO}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{OH}$	133·7	39·9

The fifteen substances given in the above series taken two at a time involve the determination of 105 thermal diagrams. A few of these have already been determined.

Since this work was begun, Pascal and Normand have published the results of investigations on similar lines (*Bull. Soc. chim.*, 1913, [iv], 13, 151, 201). They have determined the thermal diagrams for binary mixtures of the following compounds: dibenzyl, stilbene, tolane, azobenzene, and hydrazobenzene. The ten diagrams obtained show that the substances are completely miscible in the solid state. Some of the curves lie entirely between the melting points of the components; others show a minimum point.

Binary mixtures of these five substances with benzyllaniline, benzyldeneaniline, and phenyl benzyl ether have also been investigated. The thirteen diagrams obtained are all of the same form, showing a single eutectic point and limited solid-solution formation.

The thermal diagram for benzil-benzoin has been given in a previous paper (*loc. cit.*); thus, 24 of the 105 diagrams have been investigated. The present paper deals with twelve diagrams obtained from mixtures of some of the above substances with benzil and benzoin.

EXPERIMENTAL.

The method of determining the freezing points has already been described (*loc. cit.*).

About 5 grams of one of the substances were taken, and weighed quantities of the second substance added successively.

The first freezing points were observed, and also the temperature at which solidification was complete. Owing to the small quantity of substance taken and its low conductivity for heat, the accurate determination of the second temperature was often a matter of considerable difficulty.

The results are given in the following tables. In the first column is given the molecular percentages of one of the components, in the second column the first freezing points, and in the last the temperature of complete solidification.

TABLE I.

Mixtures of Benzyllaniline and Benzoin.

Benzyllaniline.	Temperature I.	Temperature II.
100.0	34.2°	—
97.13	32.2	—
86.72	68.4	32.4°
64.16	99.8	32.4
53.22	106.6	32.4
38.25	118.0	32.4
29.09	119.8	32.4
21.15	123.6	—
0.0	132.7	—

The diagram (Fig. 1) shows a eutectic point at 2.2 per cent. of benzoin at 32.4°.

TABLE II.

Mixtures of Benzylideneaniline and Benzoin.

Benzylideneaniline.	Temperature I.	Temperature II.
100·0	49·8°	—
87·45	63·8	47·0°
76·02	84·1	49·0
68·13	94·1	—
56·25	103·8	—
45·03	110·0	—
30·78	118·4	—
19·16	124·0	—
12·79	129·3	—
0·0	133·0	—

The diagram (Fig. 1) shows a eutectic point at 5·3 per cent. of benzoin at 47°.

TABLE III.

Mixtures of Dibenzyl and Benzoin.

Dibenzyl.	Temperature I.	Temperature II.
100·0	51·2°	—
93·70	59·2	50·2°
87·91	77·4	50·2
78·20	94·0	—
65·98	103·6	—
54·24	112·1	—
43·77	116·3	—
26·0	120·8	—
14·0	125·8	118·0
0·0	133·0	—

The diagram (Fig. 1) shows a eutectic at 5·5 per cent. of benzoin at 50·2°.

TABLE IV.

Mixtures of Azobenzene and Benzoin.

Azobenzene.	Temperature I.	Temperature II.
0·0	133·0°	—
9·21	127·4	121·0°
32·0	120·0	—
42·72	115·6	—
52·96	110·5	63·8
64·53	103·0	63·8
72·87	96·0	63·8
81·97	85·8	63·8
93·20	63·8	63·8
100·0	66·2	—

The diagram (Fig. 1) shows a eutectic point at 6·7 per cent. of benzoin at 63·8°.

FIG. 1.

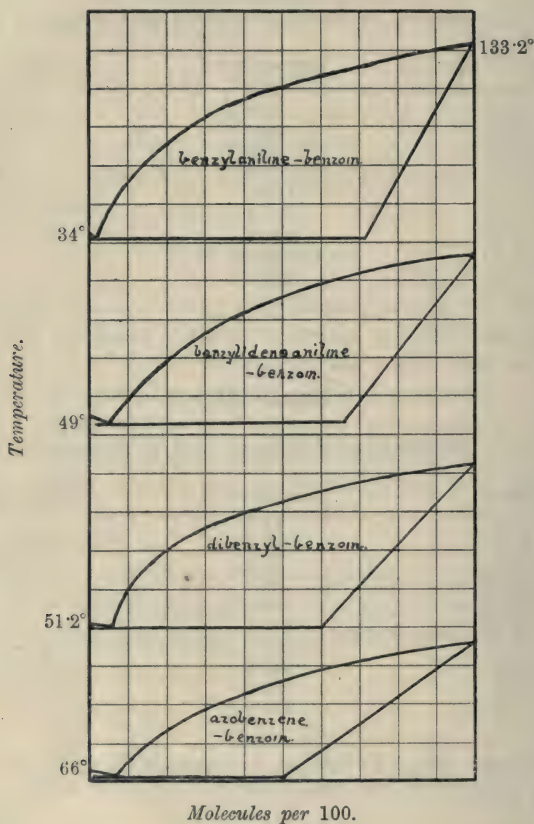


TABLE V.

Mixtures of Hydrazobenzene and Benzoin.

Hydrazobenzene.	Temperature I.	Temperature II.
0.0	133.0°	—
4.43	130.6	127.0°
22.56	122.1	98.4
40.72	110.8	98.4
53.45	100.4	98.4
64.39	100.3	98.4
83.07	116.0	98.4
100.0	127.2	—

The diagram (Fig. 2) shows a eutectic at 44.6 per cent. of benzoin at 98.4°.

TABLE VI.

Mixtures of Benzanilide and Benzoin.

Benzanilide.	Temperature I.	Temperature II.
0.0	133.0	—
11.19	128.3	123.0°
21.14	123.6	118.0
34.16	117.6	117.6
46.03	121.8	116.6
60.91	134.3	116.6
75.62	146.9	—
100.0	160.8	—

The diagram (Fig. 2) shows a eutectic point at 64 per cent. of benzoin at 116.6°.

FIG. 2.

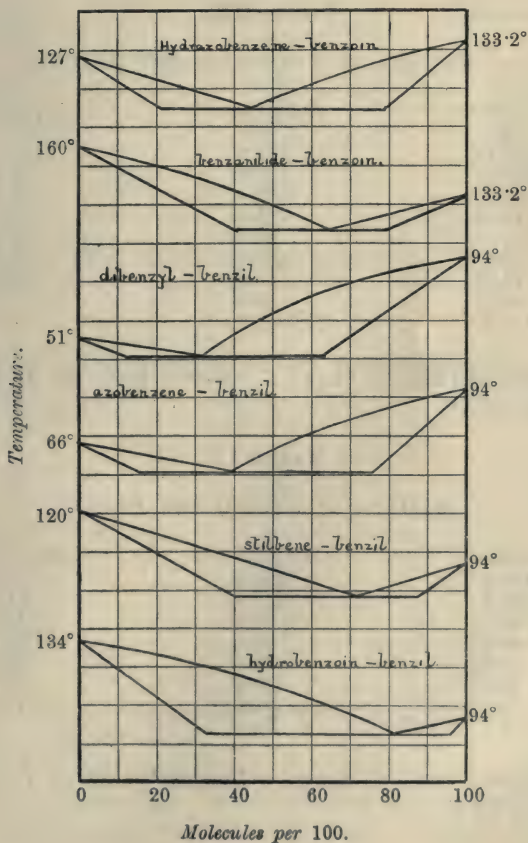


TABLE VII.

Mixtures of Benzil and Dibenzyl.

Dibenzyl.	Temperature I.	Temperature II.
100.0	51.2°	—
87.63	47.6	41.0°
76.76	42.2	41.2
74.63	41.8	41.5
61.70	51.0	41.2
56.04	57.7	42.0
47.39	66.0	41.8
35.69	74.6	—
0.0	92.7	—

The diagram (Fig. 2) shows a eutectic point at 31.8 per cent. of benzil at 41.2°.

TABLE VIII.

Mixtures of Azobenzene and Benzil.

Azobenzene.	Temperature I.	Temperature II.
0.0	92.7°	—
16.14	83.3	—
26.3	77.6	56.0°
35.4	72.6	50.5
46.26	65.3	50.3
55.0	57.0	50.3
73.57	55.0	52.0
78.25	57.0	51.5
84.07	60.5	—
100.0	66.2	—

The diagram (Fig. 2) shows a eutectic point at 39.3 per cent. of benzil at 51°.

TABLE IX.

Mixtures of Stilbene and Benzil.

Stilbene.	Temperature I.	Temperature II.
100.0	120.4°	—
77.6	110.0	94.0°
54.37	96.2	76.2
40.83	85.2	76.6
32.92	79.2	76.6
24.01	79.0	76.7
16.82	83.0	76.8
0.0	94.0	—

The diagram (Fig. 2) shows a eutectic point at 71.5 per cent. of benzil at 76.6°.

TABLE X.

Mixtures of Benzil and Hydrobenzoin.

Hydrobenzoin.	Temperature I.	Temperature II.
0 0	133·7°	—
79·29	124·6	108·0°
61·17	115·8	85·6
46·80	107·8	85·8
32·96	97·5	85·8
18·09	85·6	—
6·05	90·6	85·8
0·0	93·5	—

The diagram (Fig. 2) shows a eutectic point at 82 per cent. of benzil at 85·8°.

TABLE XI.

Mixtures of Benzil and Benzanilide.

Benzanilide.	Temperature I.	Temperature II.
100·0	160·8°	—
81·94	146·4	144·0°
60·89	132·0	87·0
45·24	119·0	87·0
29·58	101·8	87·4
21·88	93·2	87·4
14·44	87·1	87·4
12·40	88·2	87·4
0·0	93·6	—

The diagram (Fig. 3) shows a eutectic point at 85·5 per cent. of benzil at 87·4°.

TABLE XII.

Mixtures of Benzanilide and Benzylideneaniline.

Benzanilide.	Temperature I.	Temperature II.
100·0	160·8°	—
94·76	158·4	—
85·80	153·0	—
70·94	142·0	—
56·73	133·0	—
47·97	127·0	—
38·06	118·8	—
21·95	108·5	48·0°
13·64	94·6	48·0
7·11	67·0	48·5
1·79	49·8	48·0
0·0	49·8	—

The diagram (Fig. 3) shows a eutectic point at 3 per cent. of benzanilide at 48°.

The diagrams are arranged in the order of the melting points of the second component. It will be seen from those for benzoin mixtures that the eutectic point gradually shifts from one side

of the axis of concentration to the other; and that both the eutectic temperature and the concentration are dependent on the melting point of the substance mixed with benzoïn.

This is better shown in the following tables:

TABLE XIII.
Benzoïn Eutectics.

Substance.	Melting point.	Eutectic temperature.	Percentage concentration of benzoïn.
Benzylaniline	34.2°	32.4°	2.2
Benzylideneaniline	49.8	47.0	5.3
Dibenzyl	51.2	50.2	5.5
Azobenzene	66.2	63.8	6.7
Benzil	93.7	84.0	17.8
Hydrazobenzene	127.2	98.4	44.6
Benzanilide	160.8	116.6	64.0

FIG. 3.

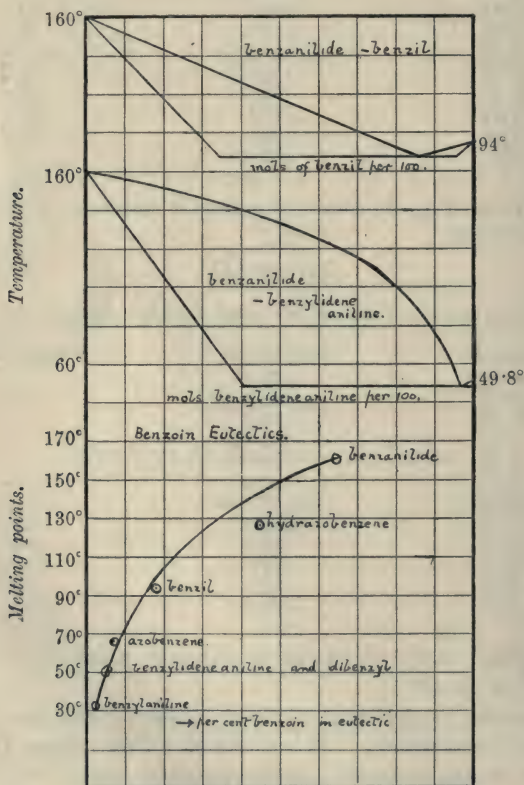


TABLE XIV.

Benzil Eutectics.

Substance.	Melting point.	Eutectic temperature.	Percentage concentration of benzil.
Dibenzyl	51.2°	41.2°	31.8
Azobenzene	66.2	51.0	39.3
Stilbene.....	120.4	76.8	71.5
Hydrobenzoin ...	133.7	85.8	82.0
Benzanilide	160.8	87.4	85.5

TABLE XV.

Benzylaniline Eutectics.

Substance.	Melting point.	Eutectic temperature.	Percentage concentration of benzylaniline.
Phenyl benzyl ether	38.5°	17.0°	55.5
Benzylideneaniline	49.8	10.0	63.5
Dibenzyl	52.5	19.0	67.5
Tolane	62.5	27.0	62.0
Azobenzene	66.2	24.7	76.5
Stilbene	123.5	32.0	95.0
Hydrazobenzene	130.5	33.0	81.0
Benzoin.....	133.2	32.4	97.8

TABLE XVI.

Benzylideneaniline Eutectics.

Substance.	Melting point.	Eutectic temperature.	Percentage concentration of benzylideneaniline.
Benzylaniline	36.0°	10.0°	36.5
Dibenzyl	52.5	30.2	72.0
Tolane	62.5	36.0	72.0
Azobenzene	66.2	33.2	77.5
Stilbene.....	123.5	45.0	92.0
Hydrazobenzene	130.5	34.2	85.0
Benzoin.....	133.2	47.0	94.7
Benzanilide	160.8	48.0	97.0

The data for tables XV and XVI have been obtained from the work of Pascal and Normand, to which reference has been made.

With the exception of tolane and hydrazobenzene (tables XV and XVI) the eutectic point always lies near the substance of lower melting point. This is well indicated by the benzylaniline eutectics. Benzylaniline has a lower melting point than any of the other substances, therefore the eutectics always contain more than 50 per cent. of benzylaniline; the greater the difference in melting points, the greater is the percentage of benzylaniline in the eutectic mixture. The exceptional behaviour of hydrazobenzene is probably explained by partial oxidation.

The eutectic rule found from the above data may be useful in approximately predicting the position of eutectic points.

It may be stated as follows:

The eutectic mixture always contains more than 50 per cent. of the constituent of lower melting point of a binary mixture; its composition depends on the difference in the melting points of the two substances; if the melting points are nearly equal, the eutectic contains approximately 50 per cent. of each; the greater the divergence, the greater is the percentage of the lower melting substance.

In the diagram (Fig. 3) the eutectic concentrations have been plotted as ordinates against melting points as abscissæ.

When binary alloys having simple eutectic diagrams are considered, it is found that the seven eutectics with tin follow the rule stated.

Of the seven bismuth eutectics those containing cadmium and silver are exceptions. The rule requires the percentage of bismuth in the cadmium-bismuth eutectic to be a little above 50, whereas it is 44.5.

The silver-bismuth eutectic has a higher percentage of bismuth than the gold-bismuth eutectic, although the melting point of gold is higher than that of silver.

In the series of lead eutectics, cadmium is again the exception.

Solid Solutions with Benzil.

It will be observed that both substances in the mixtures with benzil are symmetrical in structure and of the type $\text{Ph}\alpha\alpha\text{Ph}$. The thermal diagrams show that miscibility in the solid state with benzil mixtures is limited—never complete.

The work of Pascal and Normand (*loc. cit.*) has shown that binary mixtures of substances of the type $\text{Ph}\alpha\alpha\text{Ph}$ (in which α was one of the following: CH_2 , CH , C , N , NH) are completely miscible in the solid state.

We have then to seek for an explanation of the different behaviour of the CO-group in benzil. The explanation for miscibility suggested in a former paper (*loc. cit.*) was as follows: "The greatest degree of miscibility will be shown by two compounds when their assemblages of spheres of atomic influence possess similar marshalling, and are capable of being partitioned into units possessing almost equal volumes, these volumes being the molecular domains." Since the substances under investigation are all of the type $\text{Ph}\alpha\alpha\text{Ph}$ they possess similar marshalling.

In order to have some measure of their relative molecular domains, the molecular volumes at the temperatures of their melting points have been determined.

In some cases the density was determined by weighing a brass sphere (1) in air, (2) in water at a known temperature, (3) suspended in the fused substance at the temperature of its melting point.

In the other cases the density was determined by drawing the liquid substance up into a pipette (previously calibrated by weighing with mercury) and then weighing.

Substance.	Temperature.	Density.		Temperature.	Specific volume.	Molecular volume.
Hydrazobenzene.....	131°	1.1195	—	—	0.89325	164.4
Benzylaniline.....	36	1.0586	1.0700	33°	0.94461	172.9
Benzylideneaniline..	50	1.0450	1.0739	49	0.95691	173.3
Azobenzene.....	67	1.0498	1.0901	69	0.95258	173.8
Dibenzyl.....	52	0.9682	1.014	52	1.0328	188.0
Stilbene.....	125	0.9544	0.9707	124	1.0478	188.6
Benzil.....	94	1.1036	—	—	0.90608	190.2
Benzoin.....	134	1.0790	—	—	0.92680	196.4
Benzanilide.....	161	0.9161	—	—	1.0916	215.2
Hydrobenzoin.....	134	0.9271	—	—	1.0786	230.8

It will be observed that there are two values given for the density of some of the substances in the above table.

The second values are those obtained by Beck (*Zeitsch. physikal. Chem.*, 1904, **48**, 657); they differ considerably from the values now obtained.

Beck used the method of balancing columns of liquid in a U-tube which would fail to give accurate results.

Hydrazobenzene has a much lower molecular volume than the other substances in this series. It is worthy of notice that Beck found that the viscosities of these substances at their melting points were approximately constant (2.5) with the exception of hydrazobenzene, which had the value 2.918 (*loc. cit.*).

The substances with the greatest molecular volumes are those which contain an oxygen atom, namely, benzil, benzoin, benzanilide, and hydrobenzoin, and it is concluded that the molecular domains of these substances are greater than those of the other substances, and consequently they show more limited miscibility in the solid state. It will be observed also that the molecular volume of a saturated substance at its melting point is less than that of the unsaturated substance.

This rule has been observed previously for substances at the temperature of their boiling points (Buff, *Annalen Suppl.*, 1865, **4**, 129; Schiff, *Annalen*, 1883, **220**, 301).

Further discussion of the miscibility of substances of the type $\text{Ph}\beta\text{Ph}$ is postponed until a larger number of binary mixtures has been examined.

Summary.

(1) Binary mixtures of benzoin with compounds of the type $\text{Ph}\alpha\beta\text{Ph}$ give thermal diagrams having a single eutectic point, and forming two series of solid solutions.

The miscibility is limited—never complete.

(2) Binary mixtures of benzil with compounds of the type $\text{Ph}\alpha\alpha\text{Ph}$ and $\text{Ph}\alpha\beta\text{Ph}$ behave similarly.

(3) The position of the eutectic point (temperature and concentration) depends on the melting points of the substances. The eutectic mixture always contains a larger percentage of the constituent of lower melting point.

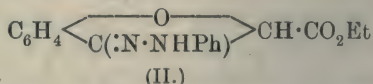
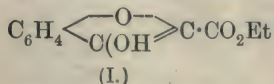
(4) It is suggested that the CO and $\text{CH}(\text{OH})$ groupings give a greater spatial domain to the molecules, and that this accounts for the more limited miscibility of benzil than of other compounds of the type $\text{Ph}\alpha\alpha\text{Ph}$.

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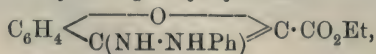
CXCIX.—*Coumaranone Derivatives. Part II. The Constitution of Ethyl Coumaranonecarboxylate.*

By RICHARD WILLIAM MERRIMAN.

SEVERAL distinct observations indicate that ethyl coumaranonecarboxylate normally exists in the enolic form (I):



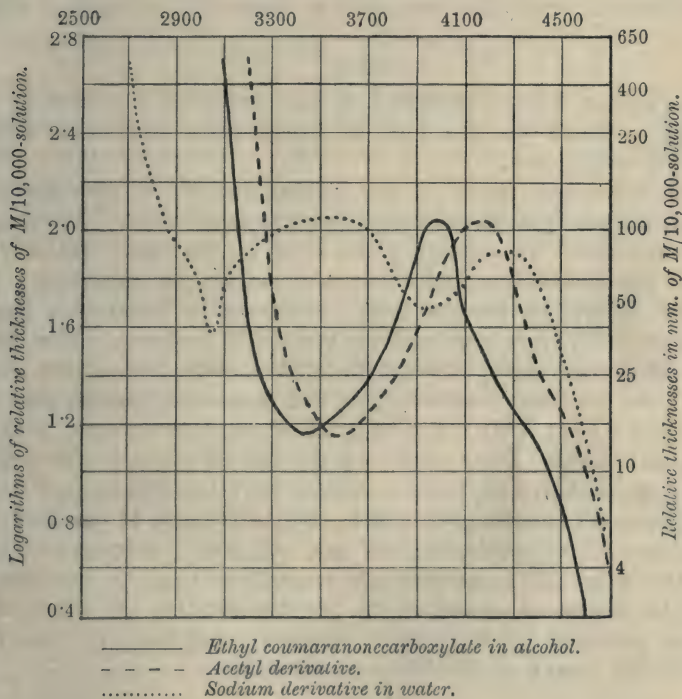
(a) Out of fifty attempts to prepare the phenylhydrazone (II), described in Part I. (T., 1911, 99, 911), by the interaction of an alcoholic solution of the ester and a solution of phenylhydrazine in 50 per cent. acetic acid, only two were successful. In all the other cases, when air was excluded an isomeric substance with entirely different properties was formed. The phenylhydrazone melts at 126° , and undergoes normal hydrolysis with alkalis and acids, and its behaviour towards light is similar to that of benzaldehydephenylhydrazone. The isomeric substance melts at 142° , is not acted on by light, and is entirely stable towards all kinds of hydrolytic agents. It is probably the phenylhydrazino-derivative,



produced from the enolic form of ethyl coumaranonecarboxylate. (b) All attempts to prepare the oxime of ethyl coumaranonecarboxylate were unsuccessful. (c) The ester is strongly acidic. On titrating its dilute alcoholic solution with *N*/10-sodium hydroxide, using phenolphthalein as indicator, exactly one equivalent of the alkali was required for neutralisation. (d) It reacts towards magnesium methiodide entirely in the enolic form. (e) Further evidence for the enolic constitution of ethyl coumaranonecarb-

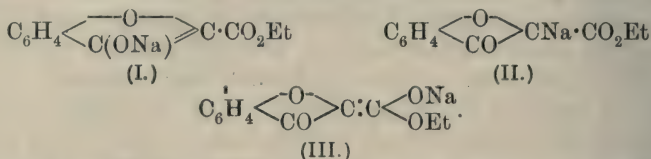
FIG. 1.

Oscillation frequencies.

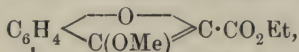


oxylate was obtained by comparing its absorption curve with that of its acetate. The curves are drawn in Fig. 1. The curve of the ester shows a deep band in the ultraviolet with its head at $1/\lambda$ 3440. The absorption curve of the acetyl derivative is parallel to the former curve throughout its length, with a slight shift towards the more refrangible end of the spectrum, the head of the band being at $1/\lambda$ 3560. The constitutions of the ester and its acetyl derivative are evidently identical, so that, assuming the ordinary formula for

acetyl compounds, the ester exists in the enolic form. Three different constitutions for the sodium derivative are possible:

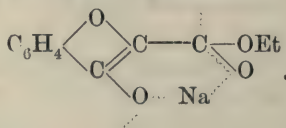


Formula (II) would not account for the intense and characteristic colour of the ferric derivative. Formula (I) receives support from the work of Auwers (*Annalen*, 1912, **393**, 338). By the action of methyl sulphate and aqueous alkali at 0° on ethyl coumaranonecarboxylate, this author obtained the *O*-methyl ether,



its formation being attributed to the action of the ions of the methyl sulphate on the ions of the sodium derivative of the strongly acidic ester.

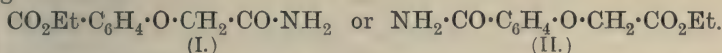
The absorption curve of the sodium derivative, also given in Fig. 1, is entirely different from the other two curves. The solution used was made by dissolving the ester in the exact quantity of dilute aqueous sodium hydroxide required for neutralisation. The general absorption for the large thicknesses of solution is moved towards the visible spectrum in the usual manner. The band present in the absorption curves of the ester and of its acetyl derivative becomes narrower and less persistent, whilst its head is shifted to $1/\lambda$ 3050. A new band of small persistency, with its head at $1/\lambda$ 3930, also appears. A similar difference in the absorption spectra of an acetyl and a sodium derivative has been observed by Hantzsch (*Annalen*, 1912, **393**, 286) in the case of the 2-alkylin-dandienes. The stable sodium salt of ethyl coumaranonecarboxylate is probably considerably ionised, so that its constitution may be expressed according to the modification of Hantzsch's theory proposed by Brannigan, Macbeth, and Stewart (this vol., p. 415) by means of the following formula:



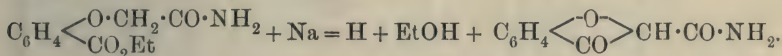
Other coumaranone derivatives react in the enolic form. For instance, Feuerstein and Brass (*Ber.*, 1904, **37**, 817) found that dihydroxycoumaranone, $\text{C}_6\text{H}_2(\text{OH})_2 \begin{array}{c} \diagup \text{O} \diagdown \\ \text{C}(\text{OH}) \end{array} \text{CH}$, did not form an oxime or a phenylhydrazone.

Attempts to prepare the amide, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{O} \\ \text{CO} \end{smallmatrix}\rangle\text{CH}\cdot\text{CO}\cdot\text{NH}_2$, by the action of alcoholic ammonia on ethyl coumaranonecarboxylate, always resulted in the formation of the ammonium salt of the ester, as was to be expected from the stability of the ester towards alkalis. The stability of ethyl coumaranonecarboxylate towards boiling alkalis is probably due to the salt formation, as Auwers (*loc. cit.*) found that the *O*- and *C*-alkyl derivatives were readily hydrolysed.

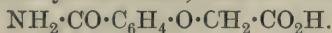
The monoamide of ethyl *o*-carboxyphenoxyacetate, previously described (Part I., T., 1911, **99**, 912), must have one of the following formulæ:



If formula (I) is correct, the monoamide should react with metallic sodium in benzene solution in the same way as ethyl *o*-carboxyphenoxyacetate, with the formation of the amide of coumaranonecarboxylic acid:

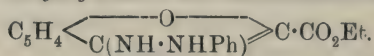


On isolating the product from the sodium salt, however, it was found to be a new amic acid with the composition $\text{C}_9\text{H}_9\text{O}_4\text{N}$. Therefore the constitution of the monoamide of ethyl *o*-carboxyphenoxyacetate probably corresponds with formula (II), so that the amic acid (*o*-carbamylphenoxyacetic acid) has the formula:



Both the original monoamide and the amic acid gave, on hydrolysis, *o*-carboxyphenoxyacetic acid, which was first prepared by Rössing (*Ber.*, 1884, **17**, 2995). The formation of the amic acid from its ester is interesting, and the method might be capable of general application. The absorption curves of the amic acid and of its ester are given in Fig. 2. They are nearly parallel to each other throughout, and the head of the band is at $1/\lambda$ 3440 in each case. A comparison of these curves with that of ethyl coumaranonecarboxylate, given in the same figure, is not without interest. The three curves are as nearly as possible parallel with each other; the head of each band is at $1/\lambda$ 3440; the three bands are of exactly the same persistence. It seems that the band might be due to the same centre of vibration in each case, the intensity being much increased in the case of ethyl coumaranonecarboxylate owing to the formation of a carbonyl group in place of a carboxyl group. The equal persistence of the three bands is certainly curious, and points to the fact that the persistence of selective absorption bands is not without physical significance (compare Dawson, this vol., p. 1311).

EXPERIMENTAL.

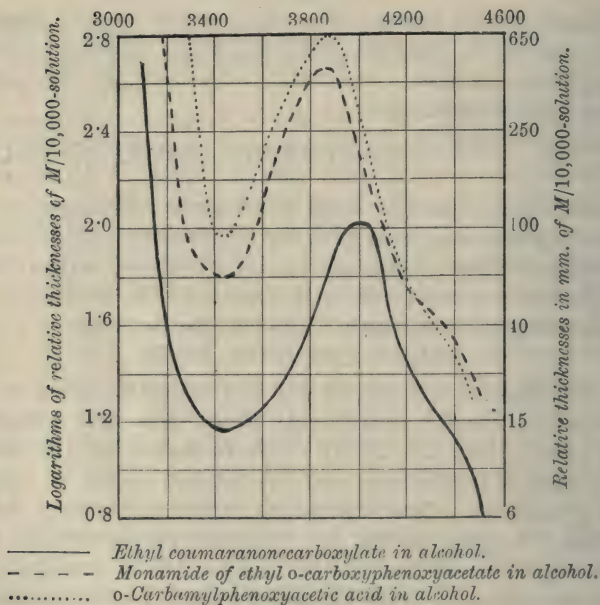
Ethyl Phenylhydrazinocoumaranonecarboxylate,

This substance was obtained during most of the attempts to prepare the phenylhydrazone of ethyl coumaranonecarboxylate.

Phenylhydrazine (1 mol.) dissolved in 50 per cent. acetic acid was mixed with an alcoholic solution of ethyl coumaranonecarboxylate (1 mol.) contained in a tightly-stoppered flask filled with

FIG. 2.

Oscillation frequencies.



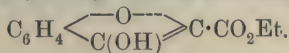
hydrogen. In the course of two days yellow crystals separated, which, when recrystallised by dissolving in acetone and adding light petroleum, were obtained in yellow leaflets melting at 142° .

This substance is insoluble in alkalis or acids, and is not hydrolysed by them even on boiling for a long time:

0.1086 gave 0.2744 CO_2 and 0.0525 H_2O . $\text{C}=68.9$; $\text{H}=5.4$.

0.2057 „ 16.8 c.c. N_2 (moist) at 14° and 763 mm. $\text{N}=9.7$.

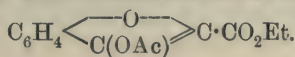
$\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_2$ requires $\text{C}=68.9$; $\text{H}=5.4$; $\text{N}=9.5$ per cent.

Titration of Ethyl Coumaranonecarboxylate,

The strongly acidic character of this ester was proved by titrating its solution in dilute alcohol with *N*/10-sodium hydroxide, using phenolphthalein as indicator:

0.2376 gram neutralised 11.6 c.c. *N*/10-NaOH. Equivalent weight=205.

$\text{C}_{11}\text{H}_{10}\text{O}_4$ requires equivalent weight=206.

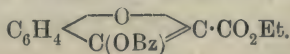
Ethyl Acetocoumaranonecarboxylate,

Ethyl coumaranonecarboxylate (3 grams) was heated with acetic anhydride (10 grams) and fused sodium acetate (3 grams) for two hours. The hot mixture was poured into hot alcohol to remove the excess of acetic anhydride. The acetyl compound, after crystallisation from dilute alcohol, separated, like the parent ester, as an emulsion, which changed into long, white needles, melting at 77°:

0.1937 gave 0.4463 CO_2 and 0.0861 H_2O . $\text{C}=62.9$; $\text{H}=4.95$.

$\text{C}_{13}\text{H}_{12}\text{O}_5$ requires $\text{C}=63.0$; $\text{H}=4.85$ per cent.

This acetyl derivative is stable towards cold alkalis.

Ethyl Benzocoumaranonecarboxylate,

Ethyl coumaranonecarboxylate was boiled for three hours with sodium benzoate and benzoyl chloride, the product being worked up in the usual way. *Ethyl benzocoumaranonecarboxylate* crystallises from light petroleum in glistening, white needles, melting at 123°, and is readily soluble in the usual organic solvents:

0.1011 gave 0.2580 CO_2 and 0.0410 H_2O . $\text{C}=69.5$; $\text{H}=4.5$.

$\text{C}_{18}\text{H}_{14}\text{O}_5$ requires $\text{C}=69.7$; $\text{H}=4.5$ per cent.

Action of Alcoholic Ammonia on Ethyl Coumaranonecarboxylate.

The ester was not attacked when boiled with alcoholic ammonia for fifteen minutes, but the *ammonium* derivative was prepared by passing ammonia into an ethereal solution of the ester. It was analysed by boiling with sodium hydroxide and collecting the ammonia in standard acid:

0.1740 neutralised 7.5 c.c. *N*/10- H_2SO_4 . $\text{NH}_4=7.8$.

$\text{C}_{11}\text{H}_9\text{O}_4(\text{NH}_4)$ requires $\text{NH}_4=8.1$ per cent.

The ammonium derivative slowly loses ammonia in the presence of water or on remaining for a long time in moist air.

Action of Grignard's Reagent on Ethyl Coumaranonecarboxylate.

The Grignard reagent, prepared by dissolving 2.4 grams of magnesium in 8 grams of methyl iodide mixed with dry ether, was slowly added to ethyl coumaranonecarboxylate (10.3 grams), dissolved in dry ether. A vigorous reaction took place, and a solid separated. The cooled mixture was treated with dilute sulphuric acid, the ethereal layer separated, and repeatedly extracted with sodium hydroxide. The alkaline extracts, when acidified, gave 10 grams of unchanged ester, showing that the ester had reacted entirely in the enolic form.

*Action of Sodium on the Monoamide of
Ethyl o-Carboxyphenoxyacetate.*

The monoamide (8 grams) was dissolved in dry benzene, and the solution added to sodium (0.84 gram) suspended in dry benzene, when a vigorous reaction took place, with evolution of gas. The reaction was completed by boiling under reflux for three hours, only a trace of ammonia being evolved during the experiment.

The solid sodium compound which separated was dissolved in much water, the solution separated from benzene, and acidified with hydrochloric acid, when a white solid was precipitated. This was only moderately soluble in the usual organic solvents; when crystallised from alcohol it formed white needles melting at 221°. For analysis it was dried at 100°:

0.1110 gave 0.2262 CO_2 and 0.0454 H_2O . $\text{C}=55.6$; $\text{H}=4.6$.

0.1835 ,, 11.3 c.c. N_2 (moist) at 17° and 763 mm. $\text{N}=7.3$.

$\text{C}_9\text{H}_9\text{O}_4\text{N}$ requires $\text{C}=55.5$; $\text{H}=4.6$; $\text{N}=7.2$ per cent.

The substance is evidently *o-carbamylphenoxyacetic acid*,
 $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

Its alcoholic solution was titrated with *N*/10-sodium hydroxide, using phenolphthalein as indicator:

0.2100 required 10.8 c.c. *N*/10- NaOH . Equivalent weight=194.4.

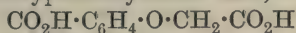
$\text{C}_9\text{H}_9\text{O}_4\text{N}$ requires equivalent weight=195.

o-Carbamylphenoxyacetic acid crystallises from acetone in very light masses having the appearance of cotton-wool, and from glacial acetic acid in clusters of small needles. It is soluble in aqueous alkalis, and is precipitated unchanged on acidifying the solutions. On adding phenylhydrazine to an alcoholic solution of the acid, heat was evolved, and a salt separated in colourless needles, which melted at 177°. This salt was decomposed by cold sodium hydr-

oxide solution with the liberation of phenylhydrazine. On acidifying the alkaline solution, the original acid, melting at 221° , was deposited.

Hydrolysis of o-Carbamylphenoxyacetic Acid.

The acid was dissolved in 10 per cent. sodium hydroxide, and the solution heated on the water-bath until ammonia ceased to be evolved. On acidifying the product, white needles slowly separated. The substance melted at 192° , and its other properties corresponded with those of *o*-carboxyphenoxyacetic acid,



(Rössing, *Ber.*, 1884, 17, 2995).

The same acid was formed by hydrolysing the monoamide of ethyl *o*-carboxyphenoxyacetate. The specimen prepared in this way also melted at 192° , and a mixture of the two melted at the same temperature

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CC.—*Coumaranone Derivatives. Part III. Acylazo-derivatives of Coumaranonecarboxylic Acid.*

By RICHARD WILLIAM MERRIMAN.

THE first known acylazo-derivative was benzoylazobenzene, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_5$, which was prepared by Emil Fischer (*Annalen*, 1877, 190, 67) by oxidising *s*-benzoylphenylhydrazine with yellow mercuric oxide. It was isolated as a dark red oil, which was decomposed by prolonged boiling with water. Benzoylazobenzene was re-examined by Hantzsch and Singer (*Ber.*, 1897, 30, 319), who found that it combined with hydrogen chloride with the formation of benzoyl-*o*-chlorophenylhydrazine.

Fischer's compound remained an isolated example of the acylazo-class of compound until the year 1905, when the present author prepared benzeneazocarbonylcoumaranone,



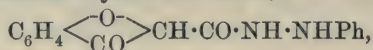
and its phenylhydrazone (Part I., T., 1911, 99, 914). These two substances and the corresponding tolyl derivatives have been subjected to more extended investigation.*

The orange azo-derivative still retains, in a greatly reduced

* Acylazo-derivatives have since been studied by Ponzio and Charrier (*Atti R. Accad. Sci. Torino*, 1909, 44, 295), Gastaldi (*Gazzetta*, 1911, 41, ii, 319) and Stollé (*Ber.*, 1912, 45, 273).

degree, the acidic properties of the parent ester. Its acetyl derivative is hydrolysed by cold alkalis, and a solution of the sodium salt is alkaline to phenolphthalein, showing that the acidic properties of the coumaranone ester have been greatly reduced by the introduction of the azo-group. The acetyl derivative is also formed when phenylhydrazine is added to an alcoholic solution of ethyl acetocoumaranonecarboxylate and the mixture exposed to the oxidising action of the air. This method of preparation is of importance, as it proves that the coumaranone residue is still present in the azo-compound, which must therefore have the constitution assigned to it.

An alkaline solution of the azo-compound is reduced by zinc dust to benzenehydrazocarbonylcoumaranone,



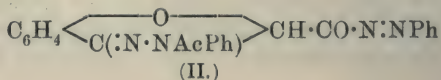
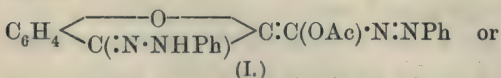
which is also produced directly by adding phenylhydrazine to an alcoholic solution of ethyl coumaranonecarboxylate in an atmosphere of hydrogen. The colourless alcoholic solution of the hydrazo-derivative is rapidly oxidised by the air, with formation of the orange azo-derivative.

It is remarkable that the ester group of ethyl coumaranonecarboxylate is attacked by phenylhydrazine, and not by alkalis or ammonia. The resistance of the ester to the latter reagents was attributed to salt-formation. This factor is absent in the case of the hydrazine, as there is no evidence of salt-formation when phenylhydrazine is added to an alcoholic solution of the coumaranone ester.

On reducing the azo-compound with stannous chloride or with sodium hyposulphite, the azo-group is broken in the normal manner, with the formation of aniline.

All the above reactions agree with the formula already proposed for the orange substance, which classes it as an acylazo-compound, but, unlike Fischer's benzoylazobenzene, it is not acted on by dry hydrogen chloride or by boiling acids or alkalis. This marked resistance to hydrolysis may be attributed to the acidic character of the substance.

The properties of the red phenylhydrazone also agree with the formula proposed for it. This substance forms an acetyl derivative which is hydrolysed by cold alkalis, the formula of which must be either



Its colour is a much paler red than that of the phenylhydrazone itself; this points to a change of constitution, so that formula (I) is the more probable. An unstable, yellow sodium derivative is formed when an alcoholic solution of sodium ethoxide is added to a benzene solution of the azo-phenylhydrazone. The acidic properties of the red substance are, however, very weak, as it is insoluble in cold alkalis. When it is boiled with 50 per cent. potassium hydroxide a small amount dissolves, and on evaporating the mixture to dryness a yellow residue of the metallic derivative is left. On acidifying the residue practically the whole of the original red substance is recovered unchanged. This marked resistance of a phenylhydrazone to alkaline hydrolysis is not without analogy. For instance, Torrey and Brewster (*J. Amer. Chem. Soc.*, 1909, **31**, 1322) found that the phenylhydrazones of aceto- α -naphthol, and of pæonol, are insoluble in potassium hydroxide, and are not hydrolysed by boiling with this reagent.

Benzeneazocarbonylcoumaranonephenylhydrazone is quite stable towards boiling concentrated hydrochloric acid, but is readily hydrolysed by fuming hydrobromic acid with loss of phenylhydrazine and formation of benzeneazocarbonylcoumaranone. There is no doubt, therefore, that the red compound is the phenylhydrazone of the orange azo-compound.

The three tolylhydrazines react with ethyl coumaranonecarboxylate in the same way as phenylhydrazine, forming colourless hydrazo-compounds, orange azo-compounds, and red hydrazones of the latter substances, which have properties exactly similar to those of the corresponding compounds already discussed.

Absorption Spectra.

If the views expressed above are correct, the colourless hydrazo-compounds and the orange azo-compounds are derived from ethyl coumaranonecarboxylate by converting a carbethoxy-group into an acylhydrazo- and an acylazo-group respectively. The absorption curve of the coumaranone ester itself shows a deep band (Part II., preceding paper, Fig. 1), so that the effect produced by the above changes on the absorption curve might be somewhat obscured. In order to get a clearer idea of the effect of such substitutions, the absorption curves of benzoic acid, *s*-benzoylphenylhydrazine, and Fischer's benzoylazobenzene were compared. The benzoylazobenzene was prepared by Ponzio and Charrier's method (*loc. cit.*), and was obtained as a dark red solid, which forms orange solutions in alcohol. The three curves are drawn in Fig. 1. The curve for benzoic acid is reproduced from a paper by Hewitt, Pope, and Willett (*T.*, 1912, **101**, 1772). This curve shows only general

absorption. In the case of *s*-benzoylphenylhydrazine the general absorption is much greater, and a very shallow band appears at $1/\lambda$ 3700. The general absorption for benzoylazobenzene reaches the visible spectrum, and the shallow band is now at $1/\lambda$ 3400.

It is clear that an acylhydrazo- or an acylazo-group does not

FIG. 2.

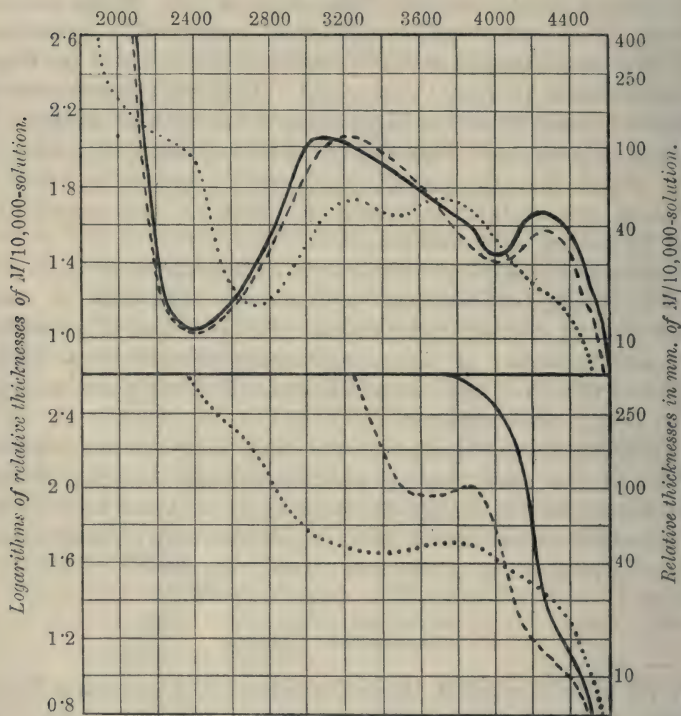


FIG. 1.

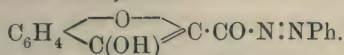
- FIG. 1. ————— Benzoic acid in alcoholic solution (reproduced).
 - - - - - *s*-Benzoylphenylhydrazine in alcoholic solution.
 Benzoylazobenzene in alcoholic solution.

- FIG. 2. ————— Benzeneazocarbonylcoumaranone in alcoholic solution.
 - - - - - Acetyl derivative in alcoholic solution.
 Benzeneazocarbonylcoumaranone in alcohol + NaOH or NaOEt.

produce a well-marked band, so that any deep band present in the absorption curves of the compounds described in this communication must be due to the coumaranone residue present in the molecule.

The absorption curves of benzeneazocarbonylcoumaranone and of

its acetyl derivative are given in Fig. 2. The two curves are practically identical, which indicates that the azo-compound exists normally in the enolic form,



The addition of alkali to the parent ester fundamentally alters

FIG. 3.

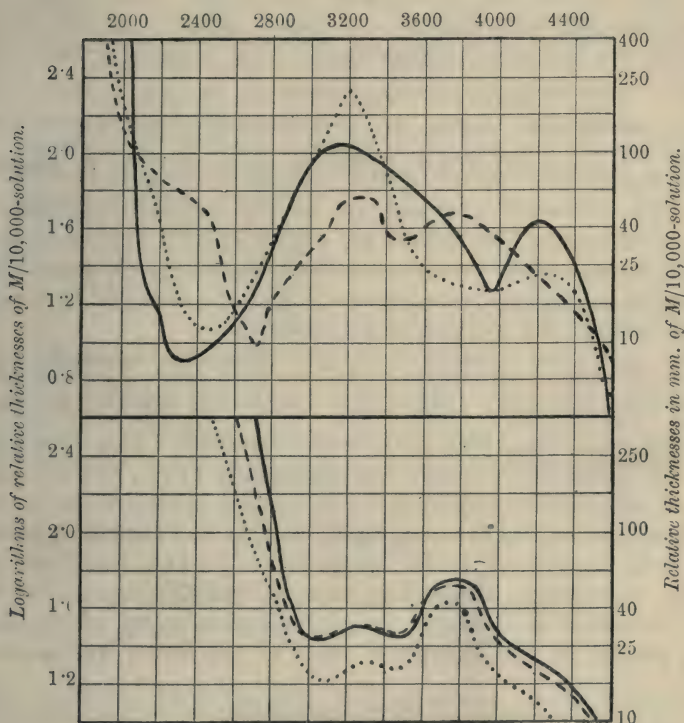
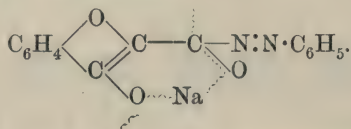


FIG. 4.

- FIG. 3. ————— *p*-Toluenecarboxylcoumaranone in alcohol.
 - - - - - " " " + NaOH or NaOEt.
 Acetyl derivative of benzeneazocarbonylcoumaranonephenylhydrazone in alcohol.
- FIG. 4. ————— Benzenehydrazocarbonylcoumaranone in alcohol.
 - - - - - " " " + NaOH.
 Ethyl hydrazinocoumaranonecarboxylate in alcohol.

the character of its absorption curve (Part II., Fig. 1). In the case of the azo-derivative also, the addition of alkali to the solution greatly alters the character of the absorption curve. The same curve, drawn in Fig. 2, is produced by adding either aqueous sodium hydroxide solution or sodium ethoxide to the alcoholic

solution of the azo-compound. The azo-derivative itself exists in the enolic form. Therefore the change in constitution, indicated by the change in the absorption spectrum, produced on adding alkali, might be explained according to the modification of Hantzsch's theory proposed by Brannigan, Macbeth, and Stewart (this vol., p. 415) by means of the formula:



The absorption curve of *p*-tolueneazocarbonylcoumaranone, $\text{C}_6\text{H}_4 \begin{array}{c} \text{---} \text{O} \text{---} \\ \diagdown \text{C} \diagup \\ \text{---} \text{C}(\text{OH}) \end{array} \text{C} \cdot \text{CO} \cdot \text{N} \text{:} \text{N} \cdot \text{C}_6\text{H}_4\text{Me}$, is given in Fig. 3, together with the alteration produced on adding sodium hydroxide or sodium ethoxide. The curves are almost exactly similar to those of the corresponding benzeneazocarbonylcoumaranone, except that the bands are slightly more persistent, and are displaced to a small extent towards the red end of the spectrum.

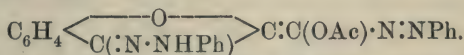
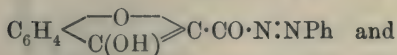
The absorption spectrum of the colourless benzenehydrazo-carbonylcoumaranone, $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} \\ \diagdown \text{C} \diagup \\ \text{CO} \end{array} \text{CH} \cdot \text{CO} \cdot \text{NH} \cdot \text{NHPh}$, is of a different type from that of the azo-derivative. The absorption curve, given in Fig. 4, shows two overlapping bands, and the addition of sodium hydroxide produces no marked change in the absorption spectrum, as was to be expected from the fact that the hydrazo-compound shows no acidic properties. It has, therefore, the ketonic constitution assigned to it above, which accounts for the great reduction in intensity, in its absorption curve, of the deep band present in the absorption curve of the enolic coumaranone ester.

The absorption curve of ethyl phenylhydrazinocoumaranonecarboxylate (Part II., *loc. cit.*), $\text{C}_6\text{H}_4 \begin{array}{c} \text{---} \text{O} \text{---} \\ \diagdown \text{C} \diagup \\ \text{---} \text{C}(\text{NH} \cdot \text{NHPh}) \end{array} \text{C} \cdot \text{CO}_2\text{Et}$, drawn in Fig. 4, is exactly similar to that of benzenehydrazocarbonylcoumaranone. The heads of the overlapping bands are at the same oscillation frequencies in the two cases, although they appear at greater dilutions in the spectrum of the hydrazino-compound. A comparison of the two formulæ assigned to these compounds explains the similarity of the selective absorption. They each contain the group $\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{NH} \cdot$, whilst neither contains an active enolic group. It is true that the coumaranone residue in the case of the hydrazino-compound has the same constitution as in the enolic compounds, $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} \\ \diagdown \text{C} \diagup \\ \text{C} \end{array}$, whilst in the hydrazo-derivative

it has the different constitution, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} \text{C}^-$. This probably accounts for the greater intensities of the vibrations in the case of the former compound.

The absorption spectrum of benzeneazocarbonylcoumaranone-phenylhydrazone could not be examined owing to the small solubility of this compound in alcohol. The absorption curve of its acetyl derivative, which was sufficiently soluble to give a $M/2000$ -solution, is given in Fig. 3. The curve is different from what one might expect, as it is very similar to that of the parent azo-compound, although no enolic group is present in the coumaranone part of the molecule.

A comparison of the formulæ given to the two compounds might explain the similarity of the absorption curves. These formulæ are:



The change in constitution of the coumaranone residue is from $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} \text{C} \cdot$ to $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} \text{C} :$, and this rearrangement has produced comparatively little change in the selective absorption.

EXPERIMENTAL.

Benzenehydrazocarbonylcoumaranone,



Ethyl coumaranonecarboxylate (1 mol.) and phenylhydrazine (1 mol.) were dissolved in alcohol (free from air), and the solutions mixed in a flask from which air had been displaced by hydrogen. The mixture became red, and after the lapse of a day a considerable quantity of colourless leaflets was deposited, which was collected and washed with dilute acetic acid. The substance was readily soluble in the usual organic solvents, but during the recrystallisation from alcohol it became slightly yellow, owing to oxidation. It was recrystallised from carbon tetrachloride in large quantity in order to minimise the risk of oxidation, and formed colourless leaflets, which melted at 140 — 141° . This substance is insoluble in dilute ammonia, and therefore does not possess acidic properties; it is slowly hydrolysed by boiling sodium hydroxide solution with the liberation of phenylhydrazine:

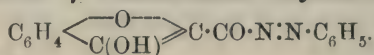
0.1974 gave 0.4851 CO_2 and 0.0770 H_2O . $\text{C}=67.0$; $\text{H}=4.3$.

0.2473 „ 22.0 c.c. N_2 (moist) at 14° and 763 mm. $\text{N}=10.6$.

$\text{C}_{15}\text{H}_{12}\text{O}_3\text{N}_2$ requires $\text{C}=67.2$; $\text{H}=4.5$; $\text{N}=10.4$ per cent.

An alcoholic solution of this compound when exposed to the air yields benzeneazocarbonylcoumaranone, and when phenylhydrazine is simultaneously present the azophenylhydrazone (Part I., *loc. cit.*) is formed.

Derivatives of Benzeneazocarbonylcoumaranone,



The *sodium* derivative is an orange powder obtained by adding sodium ethoxide to an ethereal solution of the azo-compound:

0.2518 gave 0.0610 Na_2SO_4 . $\text{Na}=7.85$.

$\text{C}_{15}\text{H}_9\text{O}_3\text{N}_2$ requires $\text{Na}=8.0$ per cent.

The *acetyl* derivative, prepared by the aid of sodium acetate and acetic anhydride, crystallises from alcohol in brownish-yellow needles melting at 187° . It is more readily soluble in alcohol or benzene than the parent compound, and is easily hydrolysed by cold alkalis. This acetyl derivative is also formed when phenylhydrazine is added to an alcoholic solution of the acetyl derivative of ethyl coumaranonecarboxylate and the mixture left exposed to the air:

0.2065 gave 0.4996 CO_2 and 0.0765 H_2O . $\text{C}=65.9$; $\text{H}=4.1$.

0.2136 „ 16.5 c.c. N_2 (moist) at 14° and 759 mm. $\text{N}=9.3$.

$\text{C}_{17}\text{H}_{12}\text{O}_4\text{N}_2$ requires $\text{C}=66.2$; $\text{H}=3.9$; $\text{N}=9.1$ per cent.

The acetyl group was estimated by Herzig's method (*Monatsh.*, 1884, 5, 90):

0.2357 gave 0.0882 BaSO_4 , corresponding with 0.0453 acetic acid.

One acetyl group would give 0.0459 acetic acid.

Reduction of Benzeneazocarbonylcoumaranone.

The azo-compound behaves towards reducing agents in the same way as azobenzene.

(a) Zinc dust was added to the hot alcoholic sodium hydroxide solution of the azo-compound until the orange-red solution became colourless. The hydrazo-derivative (*loc. cit.*) was recovered in a pure condition from this solution.

(b) On reducing the azo-compound with boiling hydrochloric acid and stannous chloride, or with sodium hyposulphite in sodium hydroxide solution, the azo-group was broken, with the formation of aniline. The other product of reduction was isolated as orange needles, which melted at 261° and sublimed without decomposition.

The substance contains nitrogen, and dissolves in concentrated sulphuric acid with the formation of a bright red solution:

0.0674 gave 0.1746 CO_2 and 0.0248 H_2O . $\text{C}=70.7$; $\text{H}=4.1$.

No simple formula can be deduced from these figures, and more of the substance is being accumulated for a complete investigation.

Derivatives of Benzeneazocarbonylcoumaranonephenylhydrazone.

The sodium derivative is an orange powder obtained by adding sodium ethoxide to the benzene solution of the azophenylhydrazone:

0.3157 gave 0.0620 Na_2SO_4 . $\text{Na}=6.35$.

$\text{C}_{21}\text{H}_{15}\text{O}_2\text{N}_4\text{Na}$ requires $\text{Na}=6.1$ per cent.

The acetyl derivative forms orange-red needles melting at 139° , and is sparingly soluble in the usual organic solvents. It is readily hydrolysed by cold alkalis:

0.1938 gave 0.4927 CO_2 and 0.0802 H_2O . $\text{C}=69.3$; $\text{H}=4.6$.

0.2059 „ 23.90 N_2 (moist) at 14° and 759 mm. $\text{N}=13.8$.

$\text{C}_{23}\text{H}_{18}\text{O}_3\text{N}_4$ requires $\text{C}=69.3$; $\text{H}=4.5$; $\text{N}=14.1$ per cent.

The acetyl was estimated by Herzig's method (*loc. cit.*):

0.3523 gave 0.1017 BaSO_4 , corresponding with 0.0523 acetic acid.

A monoacetyl derivative would give 0.0532 acetic acid.

Hydrolysis of Benzeneazocarbonylcoumaranonephenylhydrazone.

This phenylhydrazone is very resistant to hydrolytic agents. It was boiled for a day with concentrated hydrochloric acid without any hydrolytic action taking place. A large quantity was boiled with excess of 50 per cent. potassium hydroxide; the red substance gradually dissolved, and on evaporating the solution to dryness an orange-coloured residue of the potassium derivative of the red azophenylhydrazone was obtained. Hydrochloric acid was added to this residue, which was converted, apparently, entirely into the unchanged red compound; but a minute proportion of it was now soluble in dilute ammonia. The ammoniacal solution was acidified with dilute acid, and a small quantity of benzeneazocarbonylcoumaranone separated out. It was found during this work that fuming hydrobromic acid was a very powerful hydrolytic agent, and this acid readily decomposed the phenylhydrazone.

Fuming hydrobromic acid was added to the boiling alcoholic solution of the red phenylhydrazone, and the mixture boiled for twenty minutes. The alcohol was evaporated off, the residue made alkaline with sodium hydroxide, and steam blown through the mixture. Phenylhydrazine could be detected in the distillate, and the orange azo-compound was precipitated on acidifying the residue.

Similar colourless hydrazo-derivatives, orange azo-derivatives, and red azo-hydrazones were prepared by treating ethyl coumaranonecarboxylate with the three tolylhydrazines, in exactly the same way as already described in the case of phenylhydrazine.

p-Toluenehydrazocarbonylcoumaranone forms clusters of fine, colourless needles melting at 153° . It is hydrolysed by sodium hydroxide solution with the liberation of *p*-tolylhydrazine, and its alcoholic solution is oxidised by the air with the formation of the orange azo-compound:

0.1736 gave 0.4324 CO_2 and 0.0796 H_2O . $\text{C}=68.0$; $\text{H}=5.1$.

0.2253 „ 18.6 c.c. N_2 (moist) at 15° and 759 mm. $\text{N}=9.7$.

$\text{C}_{16}\text{H}_{14}\text{O}_3\text{N}_2$ requires $\text{C}=68.1$; $\text{H}=5.0$; $\text{N}=9.9$ per cent.

o-Toluenehydrazocarbonylcoumaranone forms long, colourless needles melting at 182° :

0.2573 gave 21.5 c.c. N_2 (moist) at 18° and 770 mm. $\text{N}=9.9$.

$\text{C}_{16}\text{H}_{14}\text{O}_3\text{N}_2$ requires $\text{N}=9.9$ per cent.

p-Tolueneazocarbonylcoumaranone crystallises in deep orange needles, melting at 187° :

0.1096 gave 0.2756 CO_2 and 0.0420 H_2O . $\text{C}=68.6$; $\text{H}=4.3$.

0.2315 „ 20.1 c.c. N_2 (moist) at 20° and 769 mm. $\text{N}=10.2$.

$\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_2$ requires $\text{C}=68.6$; $\text{H}=4.3$; $\text{N}=10.0$ per cent.

The *silver* derivative is a brick-red powder; the *sodium* derivative is an orange powder.

The *acetyl* derivative forms brown needles melting at 187° :

0.2418 gave 18.4 c.c. N_2 (moist) at 14° and 763 mm. $\text{N}=8.8$.

$\text{C}_{18}\text{H}_{14}\text{O}_4\text{N}_2$ requires $\text{N}=8.7$ per cent.

m-Tolueneazocarbonylcoumaranone melts at 162° , and forms a brick-red *silver* derivative, an orange *sodium* derivative, and a brown *acetyl* derivative:

0.1875 gave 0.4697 CO_2 and 0.0742 H_2O . $\text{C}=68.4$; $\text{H}=4.4$.

0.2316 „ 19.6 c.c. N_2 (moist) at 19° and 761 mm. $\text{N}=9.8$.

$\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_2$ requires $\text{C}=68.6$; $\text{H}=4.3$; $\text{N}=10.0$ per cent.

o-Tolueneazocarbonylcoumaranone forms deep orange needles melting at 193° :

0.1532 gave 0.3859 CO_2 and 0.0621 H_2O . $\text{C}=68.6$; $\text{H}=4.5$.

0.2436 „ 21 c.c. N_2 (moist) at 17° and 757 mm. $\text{N}=10.2$.

$\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_2$ requires $\text{C}=68.6$; $\text{H}=4.3$; $\text{N}=10.0$ per cent.

The *silver* derivative is a brick-red powder:

0.2736 gave 0.0779 Ag. $\text{Ag}=28.5$.

$\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}_2\text{Ag}$ requires $\text{Ag}=28.7$ per cent.

The above azo-compounds, when reduced with zinc dust and sodium hydroxide, or hydrochloric acid and stannous chloride, or

sodium hyposulphite, behave in the same way as benzeneazocarbonylcoumaranone.

p-Tolueneazocarbonylcoumaranone-p-tolylhydrazone crystallises in ruby-red needles melting at 204° :

0.2145 gave 0.5671 CO_2 and 0.1041 H_2O . $\text{C}=72.0$; $\text{H}=5.4$.

0.2518 „ 31.2 c.c. N_2 (moist) at 14° and 763 mm. $\text{N}=14.7$.

$\text{C}_{23}\text{H}_{20}\text{O}_2\text{N}_4$ requires $\text{C}=72.0$; $\text{H}=5.2$; $\text{N}=14.6$ per cent.

o-Tolueneazocarbonylcoumaranone-o-tolylhydrazone forms deep red needles melting at 173° :

0.2037 gave 0.5345 CO_2 and 0.0970 H_2O . $\text{C}=71.8$; $\text{H}=5.3$.

0.1835 „ 22.4 c.c. N_2 (moist) at 16° and 762 mm. $\text{N}=14.4$.

$\text{C}_{23}\text{H}_{20}\text{O}_2\text{N}_4$ requires $\text{C}=72.0$; $\text{H}=5.2$; $\text{N}=14.6$ per cent.

The above azohydrazones are extremely resistant to hydrolytic agents, but are hydrolysed when boiled with fuming hydrobromic acid.

This series of communications formed part of a thesis approved for the D.Sc. degree of London University.

EAST LONDON COLLEGE.

CCI.—*Condensation of Acid Chlorides with the Ethyl Esters of (a) Cyanoacetic Acid, (b) Malonic Acid, and (c) Acetoacetic Acid. Part I.*

By CHARLES WEIZMANN, HENRY STEPHEN, and
GANESH SAKHARAM AGASHE.

THE following account is an extension of a preliminary note (P., 1912, **28**, 103) on the condensation of acid chlorides with ethyl sodiomalonate, ethyl sodiocyanoacetate, and ethyl sodioacetoacetate, in which several such condensation products are described. It was thought probable that, by the preparation of this variety of substances, γ -substituted derivatives of ethyl acetoacetate might be obtained by submitting them to a suitable method of hydrolysis. With the exception of ethyl phthaliminoacetylmalonate and ethyl phthaliminopropionylmalonate, which gave ethyl phthaliminoacetoacetate and ethyl phthaliminopropionylacetate respectively when hydrolysed in the way to be described later, other condensation products led to the corresponding ketones on hydrolysis. This was the case, in particular, with the two examples described, namely,

ethyl ethoxyacetylmalonate and ethyl ethoxyacetylacetoacetate, both of which gave ethoxyacetone. Another method was therefore adopted in order to obtain ethyl γ -ethoxyacetoacetate, namely, by the condensation of ethyl acetate and ethyl ethoxyacetate, which proved to be a successful method for obtaining large quantities of this substance. In the case of ethyl phthaliminoacetoacetate, it is interesting to note that this substance has been isolated in the form of the enol- and keto-modifications. The examinations of these modifications will be pursued in the second part of this paper. Since the appearance of the preliminary note (*loc. cit.*) Pfaehler (*Ber.*, 1913, **46**, 1702) has published an account of several of the substances described by us, due to an oversight on the part of the author.*

EXPERIMENTAL.

Ethyl Ethoxyacetylcynoacetate, $\text{EtO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$.

Thirty-five grams (1 mol.) of ethoxyacetyl chloride, diluted with twice its own volume of dry ether, were added to two molecular proportions of ethyl sodiocyanoacetate (prepared by mixing 12.8 grams of finely divided sodium with 67 grams of ethyl cyanoacetate in dry ether), cooled in a freezing mixture. The mixture was allowed to remain in the cold for five hours, and then warmed gently on the steam-bath for the same period. The yellow sodium compound of the condensation product, which had separated during the reaction, was collected, washed with dry ether, and then decomposed with dilute sulphuric acid, the free condensation product being dissolved in ether. The dried ethereal extract was evaporated and the residue submitted to distillation under diminished pressure. A colourless liquid began to distil at $149^\circ/16$ mm., which gave a purple coloration with ferric chloride:

0.1334 gave 0.2670 CO_2 and 0.0826 H_2O . $\text{C}=54.44$; $\text{H}=6.8$.

$\text{C}_9\text{H}_{13}\text{O}_4\text{N}$ requires $\text{C}=54.5$; $\text{H}=6.7$ per cent.

The *copper* compound melts at 148° :

0.3402 gave 0.0572 CuO . $\text{Cu}=13.63$.

$(\text{C}_9\text{H}_{12}\text{O}_4\text{N})_2\text{Cu}$ requires $\text{Cu}=13.8$ per cent.

Ethyl Phenoxyacetylcynoacetate, $\text{PhO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$.

This is prepared, in the same way as the previous compound, from phenoxyacetyl chloride and ethyl sodiocyanoacetate. It yields a *copper* compound, melting at 191° , and the free condensation product obtained from this copper compound crystallises from light petroleum, and melts at 44° :

* Private communication.

0.1721 gave 0.4015 CO_2 and 0.0852 H_2O . $\text{C} = 63.60$; $\text{H} = 5.5$.

$\text{C}_{13}\text{H}_{13}\text{O}_4\text{N}$ requires $\text{C} = 63.16$; $\text{H} = 5.26$ per cent.

Copper compound:

0.2713 gave 0.0397 CuO . $\text{Cu} = 11.6$.

$(\text{C}_{13}\text{H}_{12}\text{O}_4\text{N})_2\text{Cu}$ requires $\text{Cu} = 11.45$ per cent.

Ethyl β -Chloropropionylcyanoacetate,
 $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$.

This is obtained by adding β -chloropropionyl chloride (1 mol.), diluted with an equal volume of ether, to ethyl sodiocyanoacetate (2 mols.), suspended in dry ether. The sodium compound of the condensation product is obtained and treated in the same way as before. The free condensation product is a white solid, crystallising from a mixture of benzene and light petroleum, and melts at 68° :

0.1852 gave 0.3220 CO_2 and 0.0867 H_2O . $\text{C} = 47.41$; $\text{H} = 5.20$.

0.1719 „ 0.1199 AgCl . $\text{Cl} = 17.2$.

$\text{C}_8\text{H}_{10}\text{O}_3\text{NCl}$ requires $\text{C} = 47.17$; $\text{H} = 4.91$; $\text{Cl} = 17.4$ per cent.

The *copper* compound crystallises from toluene in needles, melting at 159° :

0.3377 gave 0.0582 CuO . $\text{Cu} = 13.7$.

$(\text{C}_8\text{H}_9\text{O}_3\text{NCl})_2\text{Cu}$ requires $\text{Cu} = 13.50$ per cent.

Ethyl γ -Ethoxyacetoacetate, $\text{EtO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$.

This compound has been prepared by condensing ethyl acetate with ethyl ethoxyacetate by means of sodium, according to the method described by Wahl and Doll (*Bull. Soc. chim.*, 1913, [iv], **13**, 468). The substance obtained is identical with that described by Sommelet (*Compt. rend.*, 1912, **154**, 706).

γ -Oximino- α -ethoxyacetone, $\text{EtO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}:\text{NOH}$.

Ethyl γ -ethoxyacetoacetate (5.2 grams) is dissolved in a solution of potassium hydroxide (1.8 grams) in water (69 c.c.), and a solution of sodium nitrite (2.2 grams) in water (9 c.c.) is added. After being kept for twenty-four hours at the ordinary temperature, the mixture is carefully acidified with *N*-sulphuric acid. The solution is then saturated with ammonium sulphate, and the oximino-compound extracted with ether. The residue, after evaporating the dried ethereal extract, solidifies to a paste of crystals, which, on crystallising from ethyl alcohol, are obtained in fine needles, melting and decomposing at 90° . The substance is soluble in cold water or ethyl alcohol, and sparingly so in benzene or light

petroleum, from which also it can be crystallised. It dissolves in alkaline solutions with a yellow colour:

0.1050 gave 0.1749 CO_2 and 0.0629 H_2O . $\text{C}=45.44$; $\text{H}=6.66$.

0.1320 „ 12.6 c.c. N_2 (moist) at 21° and 757 mm. $\text{N}=10.84$.

$\text{C}_5\text{H}_9\text{O}_3\text{N}$ requires $\text{C}=45.8$; $\text{H}=6.87$; $\text{N}=10.7$ per cent.

Ethyl Ethoxyacetylmalonate, $\text{EtO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CO}_2\text{Et})_2$.

This compound was obtained by adding ethoxyacetyl chloride (1 mcl.), diluted with its own volume of dry benzene, to two molecular proportions of ethyl sodiomalonate, suspended in dry benzene, the mixture being cooled in ice during the addition of the chloride. After twelve hours, the mixture was warmed on the steam-bath for three hours, when the sodium compound of the condensation product separated as a yellow solid. This was collected and decomposed with dilute sulphuric acid, the free condensation product being dissolved in ether. The dried ethereal extract was evaporated, and the residue submitted to distillation under diminished pressure. The condensation product is a colourless oil, which boils at $165^\circ/19$ mm., and gives a purple coloration with ferric chloride. The copper compound crystallises from toluene or ethyl acetate in blue needles, melting at 104° , from which the free product can be obtained:

0.1711 gave 0.3338 CO_2 and 0.1135 H_2O . $\text{C}=53.2$; $\text{H}=7.36$.

$\text{C}_{11}\text{H}_{18}\text{O}_6$ requires $\text{C}=53.66$; $\text{H}=7.32$ per cent.

Copper compound:

0.2101 gave 0.0294 CuO . $\text{Cu}=11.2$.

$(\text{C}_{11}\text{H}_{17}\text{O}_6)_2\text{Cu}$ requires $\text{Cu}=11.4$ per cent.

Ethyl ethoxyacetylacetoacetate, $\text{EtO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, is prepared in a similar way to the previous compound by adding ethoxyacetyl chloride (1 mol.) to ethyl sodioacetoacetate (2 mols.) suspended in dry benzene. It is purified by means of its copper compound, and is a colourless liquid boiling at $132\text{--}133^\circ/12$ mm., and giving a purple coloration with ferric chloride:

0.0894 gave 0.1816 CO_2 and 0.0635 H_2O . $\text{C}=55.4$; $\text{H}=7.8$.

$\text{C}_{10}\text{H}_{16}\text{O}_5$ requires $\text{C}=55.4$; $\text{H}=7.4$ per cent.

The copper compound, after crystallisation from benzene, decomposes at 110° .

Behaviour of Ethyl Ethoxyacetylmalonate and Ethyl Ethoxyacetylacetoacetate on Hydrolysis in Neutral Solution.

Ten c.c. of ethyl ethoxyacetylmalonate were mixed with 5 c.c. of water, and heated in a sealed tube for one hour at 250° . The

contents of the tube were neutralised with *N*-sodium carbonate solution, and the solution was distilled in a current of steam. The distillate was saturated with potassium carbonate, and extracted several times with ether. The dry ethereal extract gave an oil, which was treated with a dilute acetic acid solution of *p*-nitrophenylhydrazine, and the *p*-nitrophenylhydrazone of ethoxyacetone was obtained, which crystallised from benzene and light petroleum in bright orange leaves, melting at 102° (*Ann. Chim. Phys.*, 1906, [viii], 9, 516).

The same result was obtained on similar treatment of ethyl ethoxyacetylacetoacetate with water in a sealed tube at 250° for one hour.

It was observed that in both cases very little acid hydrolysis had taken place, from the fact that a very small quantity of *N*-sodium carbonate solution was required for neutralisation.

Ethyl Phenoxyacetylacetoacetate, $\text{PhO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CHAc} \cdot \text{CO}_2\text{Et}$.

Phenoxyacetyl chloride and ethyl sodioacetoacetate were condensed according to the previous method; the product is best purified by means of the copper compound, from which it is obtained as an oil distilling at $174^{\circ}/14$ mm., and solidifying to a white, crystalline solid, melting at $84\text{--}86^{\circ}$; it gives the ferric chloride reaction:

0.1254 gave 0.2895 CO_2 and 0.0684 H_2O . $\text{C} = 63.6$; $\text{H} = 6.06$.

$\text{C}_{11}\text{H}_{16}\text{O}_5$ requires $\text{C} = 63.63$; $\text{H} = 6.06$ per cent.

Ethyl Amyloxyacetylacetoacetate, $\text{C}_5\text{H}_{11} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CHAc} \cdot \text{CO}_2\text{Et}$.

Molecular quantities of ethyl sodioacetoacetate and amyloxyacetyl chloride are condensed in dry ether. The product is a colourless liquid, boiling at $176^{\circ}/14$ mm., which gives a *copper* compound, and a violet coloration with ferric chloride:

0.1448 gave 0.3195 CO_2 and 0.1069 H_2O . $\text{C} = 60.1$; $\text{H} = 8.5$.

$\text{C}_{13}\text{H}_{22}\text{O}_5$ requires $\text{C} = 60.48$; $\text{H} = 8.2$ per cent.

Ethyl β -Amyloxypropionylacetoacetate,
 $\text{C}_5\text{H}_{11} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CHAc} \cdot \text{CO}_2\text{Et}$.

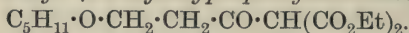
β -Amyloxypropionyl chloride (1 mol.) is condensed with ethyl sodioacetoacetate (2 mols.) in suspension in dry ether; the mixture is kept for forty-eight hours at the ordinary temperature, and then warmed for four hours on the steam-bath. It is then acidified with dilute sulphuric acid, and the condensation product dissolved in ether. After evaporating the dried ethereal extract, the residual

oil distilled at 175°/12 mm. It was purified by means of the copper compound, and is a colourless liquid:

0.1386 gave 0.3094 CO₂ and 0.1097 H₂O. C=60.88; H=8.8.

C₁₄H₂₄O₅ requires C=61.76; H=8.8 per cent.

Ethyl β-Amyloxypropionylmalonate,

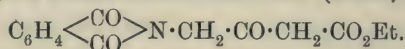


This is prepared according to the above method by condensing β-amyloxypropionyl chloride (1 mol.) with ethyl sodiomalonate (2 mols.). The substance is a colourless liquid, boiling at 190°/18 mm.:

0.1164 gave 0.2539 CO₂ and 0.0895 H₂O. C=59.51; H=8.55.

C₁₅H₂₆O₆ requires C=59.45; H=8.61 per cent.

Ethyl Phthaliminoacetoacetate (Keto-form),



This substance was prepared by condensing phthaliminoacetyl chloride (1 mol.) with ethyl sodiomalonate (1 mol.) suspended in dry benzene. After twelve hours the mixture is warmed on the steam-bath for three hours, and poured into dilute sulphuric acid until completely acidified; the benzene layer is then extracted with sodium carbonate solution several times, and the benzene afterwards removed by distillation under diminished pressure. The oily residue solidified on cooling, and on crystallisation from ethyl alcohol was obtained in small, white needles, melting at 119°. This substance does not give a coloration with ferric chloride:

0.1506 gave 0.3367 CO₂ and 0.0570 H₂O. C=61.00; H=4.3.

0.2328 „ 10.7 c.c. N₂ (moist) at 20° and 756 mm. N=5.34.

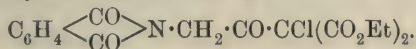
C₁₄H₁₃O₅N requires C=61.09; H=4.7; N=5.10 per cent.

Ethyl Phthaliminoacetoacetate (Enol-form).

If the alcoholic solution of the above substance is mixed with a cold alcoholic solution of an equimolecular quantity of potassium ethoxide, a yellow, crystalline potassium compound is obtained. This is dissolved in water and decomposed with cold dilute acetic acid, or by means of a current of carbon dioxide; the compound set free is dissolved in ether, and the dry ethereal extract, on evaporation, leaves a pale yellow, crystalline solid, which crystallises from ethyl alcohol in small, yellow needles, melting at 70°. This substance gives a deep purple coloration with ferric chloride, and is thus the enolic modification of ethyl phthaliminoacetoacetate:

0·1184 gave 0·2648 CO₂ and 0·0526 H₂O. C=61·00; H=4·93.
 0·1522 „ 6·4 c.c. N₂ (moist) at 15° and 765 mm. N=5·18.
 C₁₄H₁₃O₅N requires C=61·09; H=4·7; N=5·10 per cent.

Ethyl Phthaliminoacetylchloromalonate,



Phthalylglycyl chloride (1 mol.) is treated with the potassium compound of ethyl chloromalonate (1 mol.) suspended in dry benzene. The condensation product crystallises from methyl alcohol in needles, melting at 99° (Pfaehler gives 95—96°). (Found, Cl=8·93. C₁₇H₁₆O₇NCl requires Cl=9·29 per cent.)

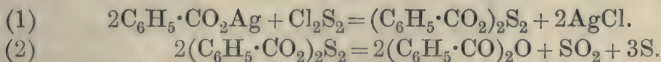
On distillation in a current of steam in presence of dilute sulphuric acid, it yields phthaliminoacetic acid.

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CCII.—*The Action of Sulphur Chloride and of Thionyl Chloride on Metallic Salts of Organic Acids: Preparation of Anhydrides.*

By WILLIAM SMITH DENHAM and HILDA WOODHOUSE
 (Carnegie Scholar).

THE preparation of anhydrides of organic acids by the action of sulphur chloride on metallic salts in the presence of an indifferent solvent has already been described by one of the authors (T., 1909, 95, 1237). The reaction proceeds in two stages, which are represented for the case of silver benzoate by the equations:

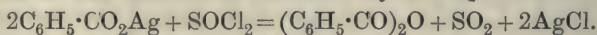


The intermediate compounds of the general formula (R·CO₂)₂S₂ can, as a rule, be isolated, but very soon decompose spontaneously in the manner indicated by equation (2).

A compound of the type (R·CO₂)₂S₂ may be regarded as a mixed anhydride of the organic acid and of an unknown sulphur acid, S₂(OH)₂, of which sulphur monochloride, S₂Cl₂, would be the chloride. Other derivatives of this acid are already known, as, for example, the substituted amides S₂(NMe₂)₂ and S₂(NEt₂)₂, which are readily obtained by the interaction of the alkylamines and

sulphur chloride (Michaelis, *Ber.*, 1895, **28**, 165). Lengfeld (*Ber.*, 1895, **28**, 449) describes esters which he terms methyl and ethyl thiosulphites, obtained by the action of sulphur chloride on sodium methoxide and on sodium ethoxide in the presence of light petroleum. The authors, although their attempts to prepare these compounds were unsuccessful and yielded only chlorinated products which evolved hydrochloric acid on keeping, propose to retain the term "thiosulphite" as a convenient designation for the acyl compounds now described.

The acyl thiosulphites should be compounds of considerable interest, and in the hope of isolating stable representatives of this class the salts of a large number of acids have been subjected to the reaction with sulphur chloride, but, despite minor variations in the degree of stability, a stable acyl thiosulphite was not obtained. The reaction, which proceeds smoothly as a rule, is, however, of general application as a method of preparing anhydrides, but fails in the cases of hydroxy- and amino-acids when more complex reactions occur, and it is inferior as a practical method to that in which thionyl chloride is used (P., 1909, **25**, 294). In this method equivalent quantities of the silver salt and thionyl chloride are shaken together in presence of ether or other indifferent solvent, when silver chloride, sulphur dioxide, and the anhydride are formed, the last-mentioned product being obtained nearly pure on filtration and removal of the solvent. The formation of benzoic anhydride in this manner is indicated by the equation:



This method also is a general one, but, as with sulphur dioxide, fails in the case of amino-acids, whilst the reaction with hydroxy-acids appears to be abnormal. The preparation of bromoacetic anhydride from the sodium salt according to this method is described in the experimental part of this paper.

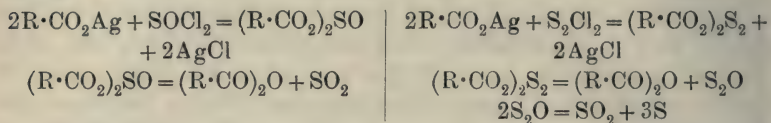
The salts of hydroxy-acids are exceptional in their behaviour towards both sulphur chloride and thionyl chloride. Sulphur chloride has little action on silver glycollate, it reacts only slowly with silver malate, whilst, with silver mandelate, reaction occurs more readily, but apparently in a less simple manner than usual. Thionyl chloride, on the other hand, reacts at once with all three salts. In the case of silver glycollate, a white, crystalline compound separates from the filtrate, the composition of which is represented by the formula $(\text{HO}\cdot\text{CH}_2\cdot\text{CO}_2)_2\text{SO}$; similar compounds are formed from silver mandelate and silver malate, although they have not been isolated in a pure condition. All these compounds part with sulphur dioxide only slowly in dry air even when they

are heated. The formation of intermediate thionyl compounds was not observed in the preparation of anhydrides of other acids by this method, and as silver methoxyacetate does not yield a thionyl compound, it appears probable that the hydroxyl group plays a specific part in the reaction when salts of hydroxy-acids are used. Jarrard, however, on applying the method to the preparation of mellitic trianhydride, noted the formation of an intermediate compound which was not decomposed at once by boiling the solution (P., 1913, **29**, 106). From the products of the reactions between thionyl chloride and the salts of these hydroxy-acids it has been found possible to separate substances of undetermined constitution which have the same percentage composition as would be possessed by anhydrides of normal type; the conditions for their preparation having now been established, their investigation will be continued. The anhydride derived from malic acid is crystalline, and appears to be a chemical individual; it differs, probably, from the substance of the same composition obtained by Walden by heating the acid. The anhydride derived from mandelic acid is a glass, and, whilst similar to the anhydrides described by Bischoff and Walden (*Annalen*, 1899, **279**, 129), Staudinger (*Ber.*, 1911, **44**, 545), and Stutz (*Ber.*, 1911, **44**, 3485), may be represented by a simpler empirical formula.

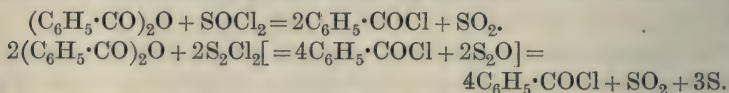
The results just recapitulated are of some interest in connexion with the much-discussed question of the constitution of sulphur chloride. At present opinion seems to be divided between the constitutions represented by the formulæ $\begin{smallmatrix} \text{S} \cdot \text{Cl} \\ | \\ \text{S} \cdot \text{Cl} \end{smallmatrix}$ and $\text{S} : \text{S} \begin{smallmatrix} \text{Cl} \\ \diagup \\ \text{Cl} \end{smallmatrix}$, the

latter representing the compound as the sulphur analogue of thionyl chloride. Although either formula is sufficient for the representation of the reactions at present under consideration, it may be pointed out, in view of the possible similarity in constitution of the two chlorides, that the analogy between the two series of reactions may be made more striking on the assumption that the first product of the interaction of the silver salt and thionyl chloride is the unstable mixed anhydride $(\text{R} \cdot \text{CO}_2)_2\text{SO}$, an assumption which finds support in Jarrard's observation just mentioned, even if the formation of a thionyl compound from silver glycollate is thought to be inadmissible as evidence on account of the possible participation of the hydroxyl groups in the reaction. Further, the intermediate compound, $(\text{R} \cdot \text{CO}_2)_2\text{S}_2$, derived from sulphur chloride may be regarded as giving as the first products of decomposition the anhydride $(\text{R} \cdot \text{CO})_2\text{O}$, and an oxide of sulphur, S_2O , which immediately decomposes into sulphur dioxide and sulphur.

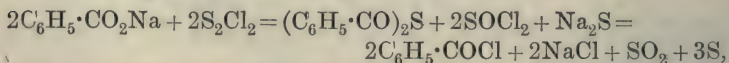
The fact that the decomposition of the acyl thiosulphite proceeds as a reaction of the first order is in harmony with this view. The changes which occur would then be represented as follows:



It may not be superfluous to point out that the analogy extends further, for, if silver benzoate is treated in the presence of ether with twice the quantity of thionyl chloride that is required for the formation of the anhydride, the filtrate, on evaporation of the solvent, gives benzoyl chloride in good yield. The preparation of acid chlorides of hydroxy-acids according to this method has been patented (Kopetschni and Karczag, Fr. Pat. 450227). Similarly, although less readily and less smoothly, sodium benzoate when heated with sulphur chloride in equimolecular proportions gives essentially benzoyl chloride, sodium chloride, sulphur dioxide, and free sulphur (Carius, *Annalen*, 1858, **106**, 291). Benzoyl chloride is formed also when benzoic anhydride is heated with sulphur chloride. The following equations represent similar reactions:



The two stages represented by the equations:



in which Carius thought the reaction between sodium benzoate and sulphur chloride to occur, appear to be less probable.

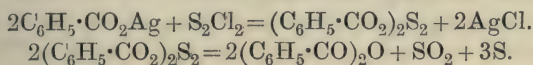
EXPERIMENTAL.

The products obtained by the action of sulphur chloride on sodium benzoate and on the silver salts of acetic, propionic, benzoic, *o*-toluic, *m*-toluic, *p*-toluic, and phenylacetic acids have already been described (T., 1909, **95**, 1235). Additional data are here given regarding the benzoyl compound, and a record of experiments with salts of other acids, which were carried out in the search for a stable compound of the type.

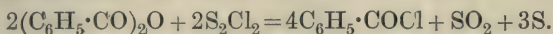
Action of Sulphur Chloride on Silver Salts.

Sulphur Chloride and Silver Benzoate.—12.5 Grams (instead of 11.5 grams) of silver benzoate suspended in 50 c.c. of dry ether

were treated with 3·4 grams of sulphur chloride, and the mixture was shaken vigorously. After filtration from the silver chloride and removal of the ether, 7·5 grams of benzoyl thiosulphite were obtained as a colourless syrup, which soon crystallised with marked evolution of heat, and afterwards decomposed. From the products of decomposition 5·6 grams of the crude anhydride were extracted by means of ether, and 0·96 gram of sulphur was left. The calculated quantities (reckoning on the amount of sulphur chloride used) are 7·6 grams of benzoyl thiosulphite, 5·65 grams of benzoic anhydride, and 0·95 gram of sulphur, if the reactions which occur are represented by the equations:



The crude anhydride was now mixed with 3·4 grams of sulphur chloride and heated under reflux for four hours. On extraction of the product with ether, 1 gram of sulphur was left, and the ethereal extract contained 6 grams of dissolved matter, which consisted chiefly of benzoyl chloride. The calculated amounts are 1·2 grams of sulphur and 7·1 grams of benzoyl chloride on the assumption that the reaction is represented by the equation:



Determination of the Velocity Constant for the Decomposition of Benzoyl Thiosulphite.

The sulphur dioxide evolved from a solution of the compound in boiling toluene was expelled from the containing flask by means of a regular current of dry carbon dioxide, and passed through a reflux condenser into a dilute solution of iodine in potassium iodide, which was replaced from time to time.

The total volume of iodine solution used (after some hours) = $a = 71\cdot2$ c.c.

Minutes.	$x = \text{c.c. Iodine.}$	$a - x.$	$1/t \log a/a - x.$
10	9·1	62·1	0·0059
26	21·4	49·8	0·0060
45	33·0	38·2	0·0060
71	43·7	27·5	0·0059
85	48·2	23·0	0·0058

Sulphur chloride and silver n-butyrate gave a viscous liquid, which closely resembled the acetyl compound:

0·3199 gave 0·6220 BaSO_4 . $\text{S} = 26\cdot71$.

0·4805, in 12·25 benzene, gave $\Delta t = -0\cdot08^\circ$. $\text{M.W.} = 213$.

$\text{C}_8\text{H}_{14}\text{O}_4\text{S}_2$ requires $\text{S} = 26\cdot89$ per cent. $\text{M.W.} = 238$.

Sulphur chloride and silver isobutyrate reacted in the usual way, but the intermediate product was so unstable that a sample could not be obtained for analysis.

Sulphur chloride and silver isovalerate gave an oil which decomposed almost immediately after preparation:

0.3437 gave 0.5954 BaSO_4 . $S=23.76$.

0.3972, in 9.07 benzene, gave $\Delta t = -0.055^\circ$. $M.W.=233$.

$\text{C}_{10}\text{H}_{18}\text{O}_4\text{S}_2$ requires $S=24.06$ per cent. $M.W.=266$.

The decomposition products from these preparations reacted immediately with aniline, giving about the same yields of anilide as is obtained from acetic anhydride.

Sulphur chloride and silver palmitate gave an intermediate product, which was only sparingly soluble in ether. The reaction mixture was therefore warmed, and, on filtering the solution, palmityl thiosulphite crystallised in soft, feathery crystals, which closely resembled those of palmitic acid:

0.2417 gave 0.2050 BaSO_4 . $S=11.64$.

0.7049, in 25.05 benzene, gave $\Delta t = -0.30^\circ$. $M.W.=469$.

$\text{C}_{32}\text{H}_{62}\text{O}_4\text{S}_2$ requires $S=11.15$ per cent. $M.W.=574$.

The compound decomposed normally, but the anhydride was not easily obtained free from sulphur.

Sulphur chloride and silver α -naphthoate gave a product which separated from the ethereal solution as a white, crystalline mass:

0.3212 gave 0.3688 BaSO_4 . $S=15.77$.

$\text{C}_{22}\text{H}_{14}\text{O}_4\text{S}_2$ requires $S=15.76$ per cent.

The anhydride presumably formed when this substance decomposed, either at the ordinary temperature or on heating, could not be obtained free from a small quantity of sulphur. After dissolving it in a solution of sodium hydroxide and filtering from the undissolved sulphur, addition of hydrochloric acid to the solution precipitated α -naphthoic acid in a pure state.

Sulphur chloride and silver monochloroacetate reacted normally, and yielded a compound which is similar to the acetyl compound, but is less stable:

0.4750 gave 0.8997 BaSO_4 . $S=26.02$.

0.649, in 10.51 benzene, gave $\Delta t = -1.57^\circ$. $M.W.=197$.

$\text{C}_4\text{H}_4\text{O}_4\text{Cl}_2\text{S}_2$ requires $S=25.50$ per cent. $M.W.=251$.

Sulphur chloride and silver tribromoacetate gave a dark brown oil, which deposited sulphur before the ether was completely removed.

Sulphur chloride and the silver bromobenzoates reacted normally. The products are probably less stable than the benzoyl compound;

for this reason and on account of its sparing solubility the para-compound was not obtained pure:

o-compound: 0.2162 gave 0.2070 BaSO₄. S=13.15.

m-compound: 0.4156 „ 0.4272 BaSO₄. S=14.11.

p-compound: 0.2350 „ 0.1730 BaSO₄. S=10.11.

C₁₄H₈O₄Br₂S₂ requires S=13.79 per cent.

Sulphur chloride and the silver nitrobenzoates react normally, and the products which, like the anhydrides themselves, are only sparingly soluble in the usual solvents, undergo normal decomposition. The reactions were carried out in the presence of carbon disulphide, and the anhydrides were extracted from the decomposition products by means of ethyl acetate, and were recrystallised from that solvent:

o-compound: 0.3352 gave 0.4194 BaSO₄. S=17.19.

m-compound: 0.1894 „ 0.2150 BaSO₄. S=15.56.

p-compound: 0.1062 „ 0.1204 BaSO₄. S=15.55.

C₁₄H₈O₈N₂S₂ requires S=16.16 per cent.

Sulphur chloride and the silver aminobenzoates react at once in presence of ether. After concentration of the yellow ethereal solution and addition of light petroleum a yellowish-brown substance is precipitated, the sulphur content of which agrees approximately with that of a substance of the formula (NH₂·C₆H₄·CO₂)₂S₂, but this compound, if formed, is not of the usual type, and although some sulphur separates on keeping, the residue still contains combined sulphur.

Sulphur Chloride and Silver Salts of Hydroxy-acids.—Reaction between sulphur chloride and silver glycollate or silver malate proceeds only slowly in the presence of ether. The products are syrups which deposit sulphur and evolve sulphur dioxide, but no definite compounds were obtained from the decomposition products. In the case of silver mandelate reaction occurs at once on the addition of an ethereal solution of sulphur chloride to a suspension of the salt in ether. After filtration from the silver chloride and removal of part of the ether by distillation, addition of light petroleum causes the precipitation of a crystalline paste, which at once decomposes with deposition of sulphur and evolution of sulphur dioxide. The only pure substance that could be obtained from the decomposition product was mandelic acid.

The behaviour of sulphur chloride towards the silver salts of the hydroxybenzoic acids appears to be irregular.

Action of Thionyl Chloride on Silver Salts.

Action of Thionyl Chloride on Silver Benzoate.—4.7 Grams of silver benzoate (instead of 4.6 grams) were treated with 1.2 grams of thionyl chloride in the presence of 30 c.c. of ether. On distillation of the ether from the filtered solution, 2.1 grams of nearly pure benzoic anhydride were obtained. The calculated amount is 2.3 grams. The method has been further tested by the preparation in a similar manner of the anhydrides of acetic, monobromoacetic, palmitic, *o*-bromobenzoic, *m*-nitrobenzoic, and α -naphthoic acids. The preparation of the anhydride of *o*-bromobenzoic acid does not appear to have been previously recorded.

Preparation of o-Bromobenzoic Anhydride.—0.6 Gram of thionyl chloride was shaken with 3.2 grams (instead of 3.1 grams) of silver bromobenzoate in the presence of 60 c.c. of ether. 1.65 Grams of a yellow, crystalline substance separated from the viscous liquid which remained after removal of the ether by distillation from the filtered solution. The calculated yield of anhydride is 1.99 grams. The yellow impurity was removed by recrystallisation from ether after treatment with animal charcoal. The anhydride melts at 75—76°:

0.1512 gave 0.1470 AgBr. Br=41.37.

$C_{14}H_8O_3Br_2$ requires Br=41.65 per cent.

Gerhardt (*Annalen*, 1853, **87**, 158) was unable to obtain *m*-nitrobenzoic anhydride in the pure state by the action of phosphoryl chloride on the sodium salt. Autenrieth (*Ber.*, 1901, **34**, 184) gives 47° as the melting point for the anhydride prepared by boiling *m*-nitrobenzoic acid with acetic anhydride. The melting point of the anhydride prepared as described below was 160°.

Preparation of m-Nitrobenzoic Anhydride.—Six grams of silver *m*-nitrobenzoate (instead of 5.5 grams) were shaken with 1.2 grams of thionyl chloride in 30 c.c. of ether. The ether was removed by distillation, and the residual mixture of silver chloride and anhydride was extracted twice by boiling with 20 c.c. of ethyl acetate each time. The crude product was recrystallised from ethyl acetate:

0.2116 gave 0.4114 CO_2 and 0.0502 H_2O . C=53.02; H=2.63.

$C_{14}H_8O_7N_2$ requires C=53.16; H=2.53 per cent.

Preparation of Bromoacetic Anhydride.—Twenty grams of thionyl chloride were added gradually to a slightly warm mixture of 55 grams of sodium bromoacetate (Bischoff and Walden, *Annalen*, 1894, **46**, 279) and 250 c.c. of dry light petroleum contained in a 500 c.c. flask fitted with a reflux condenser and a

mercury-sealed stirrer. After the vigorous reaction was over the mixture was boiled to remove the remaining sulphur dioxide, and then filtered while still warm; the residual sodium chloride was washed with ether, and further extracted for some hours with the same solvent in a Soxhlet apparatus. The combined solutions were washed with a cold aqueous solution of sodium hydrogen carbonate and dried with anhydrous magnesium sulphate. The total yield after purification by fractional distillation under diminished pressure was 80 per cent. of the calculated amount.

Thionyl Chloride and Silver Glycollate.—To 1.9 grams of silver glycollate (1 mol.) suspended in 30 c.c. of ether, 0.6 gram of thionyl chloride ($\frac{1}{2}$ mol.) was added, and the mixture shaken. The syrup left after filtration and distillation of the ether crystallised suddenly. The compound was purified by dissolving it in ether and reprecipitating with light petroleum, the process being repeated two or three times until the substance was free from halogen:

0.1984 gave 0.1796 CO_2 and 0.0536 H_2O . $\text{C}=24.69$; $\text{H}=3.00$.

0.2350 „ 0.2752 BaSO_4 . $\text{S}=15.99$.

$\text{C}_4\text{H}_6\text{O}_7\text{S}$ requires $\text{C}=24.24$; $\text{H}=3.03$; $\text{S}=16.16$ per cent.

The compound has thus the composition of a thionyl derivative of glycollic acid. The decomposition of this substance, although apparent very soon after its preparation by the odour of sulphur dioxide, does not proceed rapidly; a sample which had been left in an evacuated desiccator at the ordinary temperature still contained, nine days after preparation, 11.32 per cent. of sulphur. A small quantity of the thionyl compound which had remained for about a fortnight at the ordinary temperature was washed quickly with ether, which removed a more soluble portion, and analysed:

0.1190 gave 0.1574 CO_2 and 0.0482 H_2O . $\text{C}=36.07$; $\text{H}=4.50$.

$\text{C}_4\text{H}_6\text{O}_5$ requires $\text{C}=35.82$; $\text{H}=4.48$ per cent.

The substance has thus the composition of an anhydride of glycollic acid. It softens at about 90° , and is completely melted at $102\text{--}103^\circ$.

Thionyl chloride and silver methoxyacetate react at once without the formation of a thionyl compound. The reaction appears to proceed normally; fractional distillation of the product under diminished pressure did not, however, yield the anhydride in the pure state.

Thionyl chloride and silver mandelate in the presence of ether yield a crystalline thionyl derivative, mixed, however, with chlorinated products. If, after repeated solution in ether and reprecipitation with light petroleum, it is heated for several days at $60\text{--}70^\circ$

in a current of dry carbon dioxide to remove sulphur dioxide and then extracted with cold benzene, a glass-like product is obtained on removal of the benzene in a vacuum, which, although of undetermined constitution and possibly a mixture, has a composition nearly that of an anhydride of normal type:

0.1650 gave 0.4020 CO_2 and 0.0760 H_2O . $\text{C}=66.45$; $\text{H}=4.71$.

$\text{C}_{16}\text{H}_{14}\text{O}_5$ requires $\text{C}=67.13$; $\text{H}=4.90$ per cent.

0.5365 gram neutralised 75.3 c.c. $N/20$ -baryta solution, in which it dissolved on boiling; 70.6 c.c. would be required by the same quantity of mandelic acid, and 75.0 c.c. by an anhydride, $\text{C}_{16}\text{H}_{14}\text{O}_5$.

Thionyl Chloride and Silver Malate.—Four grams (a considerable excess) of silver malate suspended in 30 c.c. of ether were shaken with 1.2 grams of thionyl chloride. Sulphur dioxide was expelled from the filtered solution by passing carbon dioxide through it for twenty-four hours. The syrup which remained after distillation of the ether yielded a small quantity of crystalline product, which was washed with ether and analysed:

0.1169 gave 0.1732 CO_2 and 0.0372 H_2O . $\text{C}=40.44$; $\text{H}=3.54$.

$\text{C}_4\text{H}_4\text{O}_4$ requires $\text{C}=41.38$; $\text{H}=3.45$ per cent.

This *malic anhydride* softens below 70° , and is completely melted at 75 — 76° . It may be recrystallised from ether, and dissolves readily in cold water; the aqueous solution crystallises completely on evaporation in a desiccator at the ordinary temperature, yielding malic acid in an almost pure state.

The authors' thanks are due to Mr. William Dickson, who carried out a number of the above experiments, to Mr. R. Fraser Thomson for contributing an account of the preparation of bromoacetic anhydride, and to the Carnegie Trust, which has defrayed part of the cost of the investigation.

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[To face p. 1871.]

LADENBURG MEMORIAL LECTURE.

DELIVERED ON OCTOBER 23RD, 1913.

BY FREDERIC STANLEY KIPPING, D.Sc., Ph.D., F.R.S.

A MEETING of this Society which is held to commemorate the life and work of a distinguished chemist is an occasion which we approach with mingled feelings. For although we have to deplore the loss of a great man, there remain with us the recollection of his high achievements, and the example of his life worthily devoted to the advancement of knowledge.

In the minds of all chemists now living, and of all those who, in the future, trace the development of the science of our time, the name of Ladenburg is, and always will be, closely associated with the chemistry of those interesting and wonderful products of nature's laboratory, the vegetable alkaloids.

The study of some of the difficult problems presented by these complex compounds formed the main part of the experimental work of the man whose memory we honour to-day. It was a task which might well have deterred the boldest and the most sanguine spirit; but by him it was faced with persistent industry and indomitable perseverance, and brought to an issue the brilliancy of which few could have foreseen. The synthesis of *dl*-coniine, followed by the resolution of the synthetic alkaloid into its optically active components, the culminating point of these researches, was perhaps the greatest of Ladenburg's successes.

It is sometimes possible to trace the steps by which an explorer of the secrets of nature has passed from one dark region to yet another even more obscure; sometimes, however, not a single footprint remains to mark the track. In Ladenburg's case, the study of the nitrogenous products of the vegetable kingdom was preceded by an investigation of the compounds of that element which dominates the mineral world; the derivatives of benzene seem to have formed the bridge by which he crossed the gulf between those two so widely different tracts, but there is no clear record of the inspiration by which he was guided. It may have been that, while searching among the musty archives of the days long past, during the preparation of his historical work on the development of chemistry, he became fascinated by the mystery surrounding the nature and the action of those potent poisons which are elaborated by plants; the product of a common weed, even such as the deadly nightshade, which could either enhance the charms of a fair lady or lead to delirium and death, might well appeal to the imagination

of the youthful chemist, and become to him an object of absorbing scientific interest.

However this may have been, the more difficult part of the task, with which I have been entrusted, is not that of tracing Ladenburg's progress as an investigator; it is that of passing in brief review the leading personal incidents of his distinguished career.

Happily, some of the difficulties ordinarily associated with such a task have in this case been dispelled by the existence of an authentic account of many of these events from his own pen. Towards the close of his life, he suffered from severe bodily ailments, which prevented him from carrying out his official duties. It was then that, at the suggestion of his friends, and as a means of intellectual recreation, he undertook the preparation of a short autobiography. A copy of this work was very kindly lent to me by Ladenburg's second son, Dr. Rudolph, and from this authoritative source most of the following particulars have been taken.

Born of Jewish parents on July 2nd, 1842, at Mannheim, in the Grand Duchy of Baden, Albert Ladenburg was one of a family of eight, of whom, however, five died quite young. Although his parents were in a good position (his father was a *Rechtsanwalt*), and lived in a large, many-roomed house, he and his brother and sister were brought up in the old-fashioned way, and were seldom allowed in the apartments of their father and mother.

The school to which he was sent was one in which little Latin was taught, and no Greek; one reason for this choice was that his father's experience of the classical education given at the *Gymnasium* had been that it took away all desire for work. From school he went on to the *Polytechnicum* at Karlsruhe, where he applied himself industriously to the study of mathematics, modern languages, machine construction, and other subjects, and, as he himself says, tried to make good a part of what he felt had been wanting in his earlier education.

In 1860, at eighteen years of age, he went to Heidelberg, where he attended lectures at the University, and worked very diligently at home. At first he had the idea of specialising in mathematics; but he also studied chemistry under Bunsen, and later, physics, under Kirchhoff. The lectures of Bunsen, however, proved so inspiring that Ladenburg very soon went over to chemistry, and spent the livelong day in Bunsen's laboratory. Here he met, among others, C. Graebe, H. Wichelhaus (who remained his close friend for many years), C. Liebermann, Soret, and W. Preyer. He also became acquainted with Roscoe, who often visited Bunsen in those days.

During the winter session 1862-1863, Ladenburg studied in

Berlin, attending lectures by Magnus, Ranke, and others, and in the spring of 1863 he took the Ph.D. degree at Heidelberg University, *summa cum laude*, in chemistry, physics, and mathematics.

Up to this time he had devoted himself principally to inorganic chemistry, but he now began to work with Carius, who, although *Ausserordentlicher Professor* in the University of Heidelberg, had to work in a small private laboratory outside. Here it was that Ladenburg carried out his first research work, which was on a new method of elementary organic analysis, and it was during this period that he made the acquaintance of Erlenmeyer, an acquaintance which resulted in a lasting friendship.

In the spring of 1865, Ladenburg decided to go to Ghent to work under Kekulé, who at that time was at the height of his scientific activity, and had just published his first paper on the structure of aromatic compounds. At Ghent he met Körner and Glaser, who were assistants to Kekulé; he also carried out two researches on benzene derivatives, one on the "*Synthèse de l'acide anisique*," the other, in conjunction with Fitz, on "*Quelques dérivés de l'acide paraoxybenzoïque*." Except for the opportunities of intercourse with Kekulé, and with the staff and students of the laboratory—opportunities which Ladenburg prized very highly—he found life in Ghent very dull, and after a short visit to London, where he met Frankland, he proceeded to Paris. Acting on Kekulé's advice, he there interviewed Berthelot, and asked for permission to become one of Berthelot's pupils; his request was granted forthwith, but when he proceeded to inquire where he should work, he was shown a large, empty room, devoid of all fittings, of which he would be the sole occupant.

Dissatisfied with the prospect of sacrificing a considerable proportion of his time in Paris to the fitting up of this room, and of having no fellow-students with whom he could converse, in order to improve his French, he obtained an introduction to Wurtz, who was professor in the Institut de chimie, and started work in his laboratory. It was there that Ladenburg met Friedel, Caventou, Naquet, A. Gautier, and others; from Wurtz's laboratory he published with Leverkus a paper "*Ueber die Konstitution des Anethols*."

At the beginning of the winter of 1866, after spending a few months in Germany, he went, at Friedel's invitation, to work in the École des mines, where, with Friedel, he began that important series of researches on derivatives of silicon to which reference will be made again. Shortly after the commencement of this work, he was very seriously hurt by an explosion, so seriously, in fact, that his parents, who happened to be in Paris at the time, were

hardly allowed to see him. The cause of this explosion is not mentioned in his *Lebenserinnerungen*, but judging from the work described in the first paper published by himself and Friedel, it was very probably the ignition of a mixture of the vapour of silicochloroform and air. Whatever the cause of the accident may have been, as soon as he was better, he set to work again and remained in Paris during the whole of a very hot summer, in order to make up for the days lost during his temporary disablement.

Up to this time, apparently, he had not definitely chosen a profession, but now he decided to become a teacher. To this course his father consented, although he lacked faith in his son's ability. Having consulted Bunsen and Kopp in Heidelberg on the matter of his *Habilitation*, and having been informed that the original work which he had done would be accepted, Ladenburg went for a short period to Berlin, there to undertake a projected research with Wichelhaus. This collaboration led to no definite result, but his stay in Berlin was very pleasant; it gave him an opportunity of meeting Wallach, who was assistant to Wichelhaus, and also of renewing his acquaintance with Baeyer and Martius, both of whom he had previously met in Paris. At the instance of Wichelhaus, steps were then being taken to found the *Deutsche Chemische Gesellschaft*, and both Baeyer and Martius shared with Wichelhaus this important undertaking.

In January, 1868, Ladenburg successfully underwent the ordeal of his *Habilitation*, and having spent a short time in Paris, where he continued his work with Friedel, he returned to Heidelberg, in order to rent and equip a laboratory in which he could also lecture. In those days rooms were not available in the large institute occupied by Bunsen; and Erlenmeyer, Horstmann, W. Lossen, and all the chemistry *Privatdocenten* had their own laboratories outside.

At the beginning of the term, Ladenburg commenced his first course of lectures, the subject being the history of the development of chemistry during the last hundred years. He had composed the earlier lectures while he was in Paris, and later, when continuing the task at Heidelberg, he had the advantage of the advice and criticism of Erlenmeyer. It was the matter of these lectures, carefully revised, which was published in 1869 under the title, "Vorträge über die Entwicklungsgeschichte der Chemie in den letzten hundert Jahren," a comprehensive, lucid, and critical work, which passed through several editions. At the end of his four years as *Privatdocent* in Heidelberg, he was given the title of *Professor extraordinarius*. The award of this honour, it seems, had been delayed a year, a delay which Ladenburg regarded as a punishment for his having petitioned the Ministry, on behalf of

his colleagues and himself, to provide *Privatdocenten* with laboratories suitable to their work, and to allow them to attend the University lectures at nominal fees.

In 1872, he accepted, after some hesitation, the offer of the chair of chemistry in the University of Kiel. The prospects there were not attractive. On his first visit, the town itself, the University, and some of the public buildings, gave him the impression of wretchedness, an impression, however, which was afterwards modified. There was, moreover, no chemistry department; and although it was understood that one should be built and equipped in about three years, there was no place in which he could work in the meantime. Nevertheless, he finally decided to accept the professorship, and in 1873 he began to teach at Kiel in a temporary laboratory, which had been rapidly fitted up in a vacant dwelling house.

At first he had only a few students, and could give much time to his own work, although he was worried by frequently occurring committee meetings, at which there were long and acrimonious disputes among the professors, each of whom was eager to secure the best site for his own projected buildings. During this period of comparative freedom from his teaching duties, he was able to commence, in conjunction with various other chemists, the preparation of his "Handwörterbuch der Chemie," a work which was finally published in thirteen royal octavo volumes.

The new Chemistry Institute in Kiel, of which Ladenburg was appointed Rector in 1884, was not ready for occupation until the winter session of 1878-1879. Attracted by the fame of the professor, and by the lucidity and fire of his lectures, students came in rapidly increasing numbers, and soon his laboratory became crowded. While at Kiel he was responsible for passing more than twenty-five doctors of philosophy in chemistry, and it was there that he carried out many of his more important researches on the alkaloids, including the synthesis of coniine. Towards the end of his stay in Kiel, he suffered a very severe blow in the loss of his mother, to whom he was deeply attached.

In 1889, he was offered the professorship of chemistry in the University of Breslau. At first he decided to decline the call, as he found, on visiting the town, that it was devoid of all attractions, while the so-called laboratory was hardly worthy to be dignified by such a name. However, having obtained a promise that the buildings then in use should be immediately reconstructed, and that a large new Institute should very soon be erected, he accepted the chair, and took up his residence in Breslau.

At first he was very disappointed that only twenty-five students

came to work with him, and that his lectures were only very sparsely attended, but as time went on, and especially after the new Institute had been opened in 1897, the number of his students increased to such an extent that on his resignation of the chair in 1909, he had the satisfaction of having passed 160 doctors of philosophy in chemistry. Few could show such a splendid record, even in those days, when the stream of prospective German chemists was at its flood.

During his first twelve years at Breslau nothing occurred to diminish Ladenburg's mental or bodily activity, but from 1901 onwards, one great trouble quickly succeeded another. He lost his youngest son, who had been ill for many years; his relations with friends and colleagues were sorely embittered by a controversy arising out of an address entitled "*Einfluss der Naturwissenschaften auf die Weltanschauung*," delivered at the *Naturforscherversammlung* in Kassel in 1903; and in 1904 he himself became ill, and shortly afterwards had to undergo a serious operation. Although, after many months of suffering, he recovered sufficiently to be able to resume fitfully his academic duties, his health soon gave way again. The tragic loss of his eldest son, who was drowned in 1908; the death of his wife, after a most distressing illness; and his own serious ailments, led him in 1909 to tender his resignation. He died two years later, on August 15th, 1911, in his seventieth year.

A man, like Ladenburg, who, in spite of poor health, leaves a record so deeply graven on the roll of fame, must have been possessed of inexhaustible and indomitable will-power and untiring industry. Even as a youth, his devotion to his work led him to refuse the delights of a long tour in Switzerland in order to spend the time in Bunsen's laboratory; and it was by this spirit that the whole of his life was ruled.

The honours which were bestowed on him and which were earned by this stern self-sacrifice on the altar of science, were not confined to those which he received in Germany; for in addition to the title of *geheimer Regierungsrath*, the Rectorship of the University of Kiel, and the membership of the *Akademie der Wissenschaften* of Berlin, he was an Honorary and Foreign Member of this Society, a member of the *Académie des Sciences*, and correspondent for the chemistry sections of numerous other scientific societies; he was awarded the Hanbury Medal of the Pharmaceutical Society in 1902, and the Davy Medal of the Royal Society in 1907.

Well might these honours and the place which he had gained for himself in the scientific world afford him some consolation in the dark days of his closing years; but possibly they seemed to him of

little import in comparison with the glad memories of more than thirty years of happy wedded life.

His wife was Margarete, the eldest daughter of Pringsheim, professor of botany in the University of Berlin. He met her late in 1875, during a visit to the capital, and with him it was a case of love at first sight; he proposed the following Easter, and they were married on September 19th of the same year. They had three sons, of whom only one survives.

Except when writing of his relations and friends, for whom he expresses freely his deep love and affection, Ladenburg preserves in his recollections a dignified silence as to his own feelings, and a reserved modesty as to his own achievements. He does not even refer to his great "*Handwörterbuch der Chemie*," the completion of which must have given him profound satisfaction; nor is there a word to intimate the acute intellectual gratification which he must have felt when he had brought some important research to a successful issue. To a man of his devotion to science, however, the joy of adding a stone to the eternal edifice of truth must have been intense; and, though unrecorded, his feelings when he first glanced through the polarimeter tube containing his synthetic optically active coniine, might perhaps have been expressed in the words which Biot once addressed to Pasteur: "*J'ai tant aimé les sciences dans ma vie, que cela me fait battre le cœur.*"

However great may have been Ladenburg's own satisfaction on that occasion, he hastened to share it with his wife, who happened to be away from Kiel at the time; the brief telegram, "*Gretchen, es dreht,*" which he sent to her,* conveyed no doubt infinitely more than was expressed in those three words.

In spite of the reticence as to his own characteristics which pervades his *Lebenserinnerungen*, there are a few passages which throw dim sidelights on his personality. He was the kind of man we call resolute or stubborn, strong-willed or obstinate, according as his point of view agrees or disagrees with our own. When he felt himself in the right, he defended his position tenaciously, a course which involved him in litigation on more than one occasion, and which led him to publish a considerable number of polemical papers.

The unremitting attention which he gave to his academic duties left him but little time for relaxation; nevertheless, like so many of his race, he possessed musical talent of a high order, and cultivated this gift in his rare moments of leisure. In his early youth at Karlsruhe, he spent many hours at the piano; later at Heidelberg he played in quartets and other concerted music, and obtained

* Dr. Rudolf Ladenburg kindly gave me this information.—F. S. K.

a great mastery over his instrument. He was a great lover of Brahms, with whose compositions he had been made familiar by Frau Schumann, a frequent visitor at his father's house and his own. He would travel a long distance in order to hear a new work of this composer, and when at Kiel he considered it his duty to cultivate among his friends a taste for Brahms, whose music at that time was little known in the town. On several occasions he met Brahms, and had the intense pleasure of hearing that great genius interpret his own compositions.

This brief outline of Ladenburg's life, drawn by one who had not the honour of his acquaintance, must necessarily fail completely to give a picture of the living man. As this defect could not be remedied, the delineation of Ladenburg's character may be left to the more competent pen of one of his own countrymen and colleagues, the writer of the memorial published in the *Berichte*.

When in 1866 Ladenburg was invited by Friedel to go and work in Paris on compounds of silicon, only a few organic derivatives of that element were known; those containing a silicon atom directly united to a carbon atom could, in fact, be counted on the fingers of one hand. If this state of knowledge is contrasted with that which obtained in 1883, when Beilstein's "Handbuch der organischen Chemie" was first published, some idea may be gained of the progress which had been made during the intervening years. This great advance was principally due to those researches which, commenced with Friedel, were continued by Ladenburg alone, and which formed, not the very first, but one of the earlier chapters of the latter's scientific record.

The first joint communication, published in 1867 (*Annalen*, **143**, 118), contained an account of silicochloroform. Some ten years previously Buff and Wöhler had heated crystalline silicon in a stream of dry hydrogen chloride, and had obtained a liquid to which they had given the formula $\text{Si}_2\text{Cl}_3 + 2\text{HCl}$ ($\text{Si} = 21$); this formula was subsequently altered by Wöhler to $\text{Si}_6\text{Cl}_{10}\text{H}_4$ ($\text{Si} = 14$), but he recognised the fact that he had been unable to obtain the liquid in a pure state, and that consequently its formula was not definitely established. Friedel and Ladenburg prepared this compound in a state of purity, and proved it to have the molecular formula SiHCl_3 ; its further study led them to the discovery of several interesting and novel reactions. One of its derivatives, namely, triethyl ortho-silicoformate, which was obtained by treating the trichloro-compound with ethyl alcohol, underwent a remarkable decomposition when it was warmed with sodium; the metal remained unchanged, but the ester was decomposed, giving pure silicomethane, SiH_4 , and

an ester of orthosilicic acid, a change which is expressed by the following equation: $4\text{SiH}(\text{OEt})_3 = \text{SiH}_4 + 3\text{Si}(\text{OEt})_4$.

This reaction, which is comparable to the decomposition by heat of the lower acids of phosphorus into phosphine and orthophosphoric acid, passed into the text-books of inorganic chemistry as a method for the preparation of pure silicomethane, and the equation just given has certainly been committed to memory, for examination purposes, by many puzzled students, who had not the remotest idea of the nature of triethyl orthosilicoformate.

As silicomethane had not until then been prepared in a pure state, Friedel and Ladenburg established its composition, and found that the pure gas was not spontaneously inflammable in air at the ordinary temperature and pressure, but was so under lower pressures. In addition to silicochloroform, they investigated other purely inorganic silicon compounds, more particularly silicon oxychloride, $\text{SiCl}_3 \cdot \text{O} \cdot \text{SiCl}_3$, which they prepared by passing the vapour of silicon tetrachloride through a white hot porcelain tube (*Ber.*, 1868, **1**, 86); although unable to discover how this compound was produced, they proved that it reacted with alcohol, giving the ethoxy-derivative, $\text{Si}(\text{OEt})_3 \cdot \text{O} \cdot \text{Si}(\text{OEt})_3$, and with zinc ethyl at 180° , giving silicoethyl oxide, $\text{SiEt}_3 \cdot \text{O} \cdot \text{SiEt}_3$.

The only method available in those days for bringing about the direct union of silicon and carbon was to heat silicon tetrachloride with zinc alkyls in sealed tubes. By using sodium in conjunction with the zinc compound, Friedel and Ladenburg succeeded in bringing about the displacement of the chlorine by an alkyl group at much lower temperatures and without the use of sealed tubes (*Ber.*, 1870, **3**, 15). In this way they prepared triethyl orthosilicopropionate, $\text{SiEt}(\text{OEt})_3$, from triethoxysilicic chloride, which was itself obtained by the interaction of silicon tetrachloride and ethyl alcohol.

This ester was not completely hydrolysed by alcoholic potash in the cold, and when boiled with a concentrated aqueous solution of the alkali, it gave a product which had only approximately the composition $\text{EtSiO} \cdot \text{OH}$. For the preparation of the pure acid the ester was heated in sealed tubes with acetic chloride, and the product, ethylsilicon trichloride, SiEtCl_3 , was hydrolysed with water. Silicopropionic acid, $\text{EtSiO} \cdot \text{OH}$, was thus obtained as an amorphous powder; it was the first representative of the silicon analogues of the carboxylic acids. Although, later on, Ladenburg prepared silicoacetic acid, $\text{MeSiO} \cdot \text{OH}$ (*Ber.*, 1873, **6**, 1029), and silicobenzoic acid, $\text{PhSiO} \cdot \text{OH}$, and several compounds supposed to be of this type have been obtained in recent times, little is known of their nature: except for the fact that such acids give soluble potassium salts,

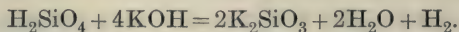
they are extremely inert, and behave in every respect differently from the carboxylic acids.

The discovery of silicopropionic acid raised in Ladenburg's mind a question which, some years afterwards, he attempted to solve (*Ber.*, 1872, **5**, 568), namely, whether the silicon which is contained in plants is in combination with carbon or is a constituent of a purely mineral silicate. This problem, apparently, is still awaiting solution.

The main object of the joint researches just referred to was to gain some information as to the extent of the analogy between compounds of silicon and carbon; to ascertain whether the new theories which were just then being developed in connexion with organic compounds could also be applied to the so-called inorganic elements, or whether, as some believed, these new theories were both "unnütz und verwirrend."

As a further step in this direction, Friedel and Ladenburg (*Bull. Soc. chim.*, 1867, [ii], **7**, 65) attempted the synthesis of a quaternary hydrocarbon, and succeeded in obtaining dimethyldiethylmethane, CMe_2Et_2 , the first known compound of this type; the existence of this hydrocarbon proved that the carbon atom, like the silicon atom in Friedel and Craft's tetraethylsilicane, SiEt_4 , could unite directly with four hydrocarbon radicles.

They next tried to obtain a compound in the molecule of which two silicon atoms were directly united, as are the carbon atoms in ethane; after many fruitless attempts they finally succeeded (*Bull. Soc. chim.*, 1869, [ii], **12**, 92; *Annalen*, 1880, **203**, 241) in preparing silicoethane, $\text{SiEt}_3\cdot\text{SiEt}_3$, in the following manner: Silicon tetraiodide was heated with molecular silver at about 300° , and was thus converted into the hexaiodide, Si_2I_6 (from which the corresponding bromide, Si_2Br_6 , and chloride, Si_2Cl_6 , were prepared). The hexaiodide was hydrolysed with ice-cold water, yielding an amorphous product, silico-oxalic acid, $\begin{array}{c} \text{SiO}\cdot\text{OH} \\ | \\ \text{SiO}\cdot\text{OH} \end{array}$, which showed an interesting behaviour; when heated in the air, the acid was decomposed into silica and hydrogen; when warmed with potassium hydroxide it gave potassium metasilicate with evolution of hydrogen:



The interaction of silicon hexaiodide and zinc ethyl took place very readily, giving a colourless liquid, boiling at 250 — 253° , which was proved to be the desired compound, hexaethylsilicoethane, $\text{SiEt}_3\cdot\text{SiEt}_3$.

During the preparation of triethyl silicoformate from triethylsilicic chloride, Friedel and Ladenburg had observed the formation

of diethoxydiethylsilicane, $\text{SiEt}_2(\text{OEt})_2$, as a by-product. This observation led Ladenburg to study the action of zinc ethyl and sodium on ethyl orthosilicate, $\text{Si}(\text{OEt})_4$. In a series of papers (*Ber.*, 1871, **4**, 727, 901; 1872, **5**, 565, 1081) he showed that the ethoxy-groups in this ester might be successively displaced by ethyl radicles, giving the compounds $\text{SiEt}(\text{OEt})_3$, $\text{SiEt}_2(\text{OEt})_2$, $\text{SiEt}_3\cdot\text{OEt}$, and SiEt_4 , as well as triethylsilicane, SiEt_3H .

The diethoxydiethyl derivative, $\text{SiEt}_2(\text{OEt})_2$, could not be hydrolysed to the corresponding dihydroxy-compound with alcoholic potash, but when heated with acetyl chloride in sealed tubes it gave the halogen derivatives $\text{SiEt}_2(\text{OEt})\text{Cl}$ and SiEt_2Cl_2 ; the latter, with water, yielded a thick syrup, which Ladenburg regarded as silicon diethyl ketone, or oxide, SiEt_2O , but the analytical results did not agree well with those required for this formula.

The monoethoxy-derivative was hydrolysed by hydriodic acid, but gave the oxide $\text{SiEt}_3\cdot\text{O}\cdot\text{SiEt}_3$; when heated at 180° with acetyl chloride, it was converted into silicoheptyl chloride, SiEt_3Cl , which, with ammonia, gave silicoheptyl alcohol, $\text{SiEt}_3\cdot\text{OH}$. This was the first known silicon derivative of the alcohol type, and for this and analogous compounds, Ladenburg proposed the class name "sili-cole," corresponding with Kolbe's "carbinole."

A few silicon derivatives containing aromatic radicles were also prepared, as, for example, phenylsilicon trichloride, SiPhCl_3 , which was obtained by heating silicon tetrachloride with mercuric phenyl (*Ber.*, 1873, **6**, 379). This trichloride and the ester, $\text{SiPh}(\text{OEt})_3$, prepared from it, gave on hydrolysis products which seemed to be identical, and which were believed to be silicobenzoic acid, $\text{PhSiO}\cdot\text{OH}$.

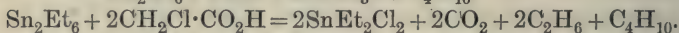
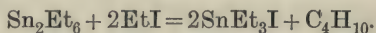
Some thirty years later Ladenburg's thoughts again turned to these aromatic silicon compounds, and he prepared various derivatives of silicon tetraphenyl (*Ber.*, 1907, **40**, 2274), but apparently his attempts to sulphonate triphenylsilicol were not successful (*Ber.*, 1908, **41**, 966).

This short summary of Ladenburg's researches on silicon compounds can give little idea of the very great experimental difficulties with which he had to contend, and of the time which he must have devoted to these investigations. But in spite of the exacting character of this work, during its progress he was also able to study some organic compounds of tin.

The object here was not, as might have been expected, to establish some analogy between tin and silicon; it was to try and find out whether the molecule of a stannous compound contained one or two atoms of tin. In his opinion, the *ous* compounds of iron, manganese, chromium, and other metals contained two atoms of the

metal in their molecules (*Ber.*, 1869, **2**, 706), but experiments with certain inorganic iron, manganese, and tin compounds failed to give any evidence in support of this view. He therefore prepared "stanntriäthyl," a compound which had been obtained by Cahours, but the formula of which had not been established. This ethyl derivative was proved to have the composition, Sn_2Et_6 , and the fact that two atoms of tin could unite directly was thus established, although the molecular structure of stannous compounds still remained unknown (*Ber.*, 1870, **3**, 353).

From the hexaethyl derivative Ladenburg prepared various other organic tin compounds; he showed that it was decomposed by iodine, giving tin triethyl iodide, SnEt_3I , from which, with the aid of sodium and bromobenzene, he obtained tin phenyltriethyl, SnEt_3Ph (*Ber.*, 1871, **4**, 17). He also found (*Ber.*, 1871, **4**, 19) that the hexaethyl compound underwent the following interesting decompositions:



A much more important chapter of Ladenburg's work is that containing his numerous contributions, both theoretical and practical, on benzene and its derivatives. That a young and enthusiastic chemist, who had worked in Kekulé's laboratory, would take an active part in the solution of the many interesting problems suggested by the theory of the structure of benzene was, of course, only to be expected; it was merely a question of how far his own efforts would meet with success.

As a matter of fact, of the many who assisted in the examination of the fundamental propositions of the aromatic theory, few played a more prominent part than Ladenburg, or brought perspicacity and critical acumen of a higher order to the discussion of the experimental data. His first researches on aromatic compounds, carried out in Kekulé's laboratory and published in 1866-1867, have already been mentioned. During the next two years, although fully occupied with silicon compounds in the laboratory, his mind was evidently running on the aromatic theory, and as early as 1869 he contributed a paper in which he had the temerity to criticise Kekulé's formula, and to suggest alternatives, among which occurred the now well-known prism formula, originally put forward by Claus.

In this paper (*Ber.*, 1869, **2**, 272) Ladenburg showed that whereas, according to Kekulé's formula, the positions 1:2 and 1:6 must be, and the positions 1:3 and 1:5 may be, different, certain experimental data of Hübner and Petermann pointed strongly to the contrary conclusion, namely, that in the benzene

nucleus there are two hydrogen atoms which are symmetrically situated with respect to a third such atom. The argument was as follows: *m*-Bromobenzoic acid gives two bromonitrobenzoic acids, which, on reduction, are converted into the same aminobenzoic acid. The nitro-groups in the bromonitro-acids must have displaced two hydrogen atoms, which are differently situated with regard to the bromine atom, but identically situated with respect to the carboxyl group. Therefore either the position 1 : 2 = 1 : 6, or 1 : 3 = 1 : 5.

A few years later (*Ber.*, 1872, **5**, 322) he discussed the isomerism of benzene derivatives. The view that only three di-substitution products could be obtained was at that time supported by negative evidence only; no more than three such isomeric compounds had ever been prepared. From data established by Carstanjen (*J. pr. Chem.*, 1871, [ii], **3**, 50) in an experimental investigation of hydroxythymoquinone, Ladenburg not only deduced important conclusions regarding the symmetry of the benzene molecule, but also argued from Carstanjen's facts that only three di-substitution products of benzene were theoretically possible.

Two papers on pentachlorobenzene (*Ber.*, 1872, **5**, 789; 1873, **6**, 32) may next be mentioned, as they illustrate the experimental skill with which Ladenburg overcame a very difficult practical problem.

Two pentachlorobenzenes had been described, the one by Otto, the other by Jungfleisch. As the result of a most laborious investigation, involving hundreds of fractional crystallisations (*Annalen*, 1874, **172**, 331), Ladenburg was able to show that the supposed isomerides did not exist, and that a statement which could not be reconciled with the "Gleichwertigkeit" of the six hydrogen atoms of benzene had no foundation in fact.

In his work on mesitylene, which was published shortly afterwards (*Ber.*, 1874, **7**, 1133; *Annalen*, 1875, **179**, 163), he proved that the three displaceable hydrogen atoms in this hydrocarbon were all "gleichwertig," and consequently that mesitylene was symmetrical trimethylbenzene.

The proof was as follows: Dinitromesitylene, which may be represented by the formula $C_6Me_3\overset{a}{H}\overset{b}{NO_2}\overset{c}{NO_2}$, was converted into nitromesidine, $C_6Me_3\overset{a}{H}\overset{b}{NO_2}\overset{c}{NH_2}$, by reduction, and the acetyl derivative of this base was transformed into dinitracetmesidine, $C_6Me_3\overset{a}{NO_2}\overset{b}{NO_2}\overset{c}{NHAc}$. This compound was hydrolysed, and the dinitroamino-derivative converted into a dinitromesitylene, $C_6Me_3\overset{a}{NO_2}\overset{b}{NO_2}\overset{c}{H}$, by Griess' method. The substance thus obtained

was identical with the original dinitromesitylene; therefore two of the displaceable hydrogen atoms, a and c , are "gleichwertig."

The nitromesidine, $\text{C}_6\text{Me}_3\overset{a}{\text{H}}\overset{b}{\text{NO}_2}\overset{c}{\text{NH}_2}$, obtained from the dinitromesitylene, $\text{C}_6\text{Me}_3\overset{a}{\text{H}}\overset{b}{\text{NO}_2}\overset{c}{\text{NO}_2}$, gave the mononitro-derivative, $\text{C}_6\text{Me}_3\overset{a}{\text{H}}\overset{b}{\text{NO}_2}\overset{c}{\text{H}}$, when the amino-group was displaced by hydrogen. The nitro-compound was then reduced to mesidine, acetylmесidine was nitrated, and the product was hydrolysed to a nitromesidine, $\text{C}_6\text{Me}_3\overset{a}{\text{NO}_2}\overset{b}{\text{NH}_2}\overset{c}{\text{H}}$, or $\text{C}_6\text{Me}_3\overset{a}{\text{H}}\overset{b}{\text{NH}_2}\overset{c}{\text{NO}_2}$; but since $a=c$, these formulæ are identical. Since, moreover, this nitromesidine was identical with that, $\text{C}_6\text{Me}_3\overset{a}{\text{H}}\overset{b}{\text{NO}_2}\overset{c}{\text{NH}_2}$, obtained from dinitromesitylene, $b=c$, and therefore $a=b=c$. He frankly recognised that the fact that mesitylene was symmetrical trimethylbenzene afforded strong evidence against the prism formula, and he concluded therefore that "there is at the present time no symbolic representation of benzene which satisfies all requirements."

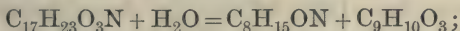
Another paper which has become a classic is that in which Ladenburg showed that in the benzene nucleus there were at least four hydrogen atoms which were identically situated (*Ber.*, 1874, 7, 1684). His proof, which is of such fundamental importance that it is given in most of the test-books of organic chemistry, was the following. Phenol, treated with phosphorus pentabromide, gave bromobenzene, from which, with the aid of sodium and carbon dioxide, benzoic acid was obtained. Now benzoic acid was known to give rise to three isomeric hydroxybenzoic acids, $\text{C}_6\text{H}_4(\text{OH})\cdot\text{CO}_2\text{H}$; in each of these compounds the hydroxyl group must have displaced a different hydrogen atom from the benzene nucleus, and none of these hydrogen atoms was identical with that displaced by the hydroxyl group in the original phenol. All three hydroxybenzoic acids were converted into a phenol and carbon dioxide; the phenol thus obtained was in every case identical with the original compound.

The substance of Ladenburg's more important contributions to the chemistry of benzene is to be found in his "Theorie der aromatischen Verbindungen," published in 1876, a few years after he went to Kiel. In this monograph he gave a critical review of the position of the aromatic theory at that time, and also did a great service to chemistry by drawing attention to the importance of Körner's method for the orientation of benzene derivatives.

Various other researches on aromatic compounds, including those on the aldehydine bases (*Ber.*, 1878, 11, 590, 1648; see also *Ber.*, 1878, 11, 1653, 1656), were carried out between 1876 and 1878,

but in the following year he began his study of the alkaloids and related compounds, a task which, with its side issues, occupied him almost exclusively during the rest of his working life.

In those days there were known various vegetable products, which were used in medicine for different purposes, but had in common the remarkable property of dilating the pupil of the eye. Among these alkaloids were belladonine and atropine, obtained from the deadly nightshade (*Atropa belladonna*), henbane, or hyoscyamine, from *Hyoscyamus niger*, duboisine, from *Duboisia myoporoides*, and daturine, from *Datura stramonium*. The only one of these substances that had been investigated other than very superficially was atropine; Lossen had shown that this base was hydrolysed by concentrated hydrochloric acid, giving tropine and tropic acid:



from tropic acid, atropic acid, $\text{C}_9\text{H}_8\text{O}_2$ (and isotropic acid) had been obtained, and atropic acid had been reduced to hydratropic acid, $\text{C}_9\text{H}_{10}\text{O}_2$.

Ladenburg first succeeded in preparing atropine from its decomposition products by evaporating a dilute hydrochloric acid solution of tropine with tropic acid (*Ber.*, 1879, **12**, 941); he found that this artificial atropine was identical with the natural product in every respect, including its physiological action.

He then showed that tropine reacted with other organic acids in a similar manner, in presence of hydrochloric acid, giving compounds which he named tropeines (*Ber.*, 1880, **13**, 1081; 1882, **15**, 1025); of these, the product from tropine and mandelic acid, phenylglycolytropeine, or homatropine, $\text{C}_{16}\text{H}_{21}\text{O}_3\text{N}$, had a mydriatic action not quite so strong as, but much more rapid than, that of atropine; homatropine, moreover, was less poisonous than atropine. This partially synthetic alkaloid found application in ophthalmic surgery.

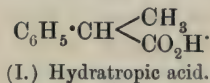
The results of the further investigation of atropine were published in numerous papers during 1880–1882, and were briefly as follows: Hydratropic acid, $\text{C}_6\text{H}_5\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, oxidised with permanganate (Ladenburg and Rügheimer, *Ber.*, 1880, **13**, 373), gave an acid, $\text{C}_9\text{H}_{10}\text{O}_3$, which was identical with the atrolactic acid obtained by Fittig and Wurster (*Annalen*, 1879, **195**, 145) by treating atropic acid with hydrobromic acid and hydrolysing the product; this fact showed that atrolactic acid had not the constitution $\text{C}_6\text{H}_5\cdot\text{CH}(\text{CH}_2\cdot\text{OH})\cdot\text{CO}_2\text{H}$ assigned to it by Fittig and Wurster, but $\text{C}_6\text{H}_5\cdot\text{C}(\text{OH})(\text{CH}_3)\cdot\text{CO}_2\text{H}$. Atrolactic acid, heated with hydrochloric acid, was converted into atropic acid; the latter

combined with hypochlorous acid to form a chlorohydroxy-acid, from which tropic acid was obtained when the chlorine was displaced by hydrogen.

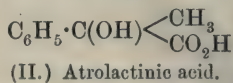
These results showed that tropic acid was not



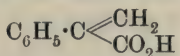
as suggested by Fittig and Wurster, and that the relationship between the four acids just mentioned was as follows:



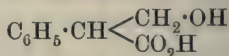
(I.) Hydratropic acid.



(II.) Atrolactic acid.



(III.) Atropic acid.



(IV.) Tropic acid.

The synthesis of tropic acid was then accomplished in conjunction with Rüchheimer (*Ber.*, 1880, **13**, 2041). Acetophenone dichloride, boiled with potassium cyanide in alcoholic solution, gave the compound $\text{C}_6\text{H}_5 \cdot \text{CMe}(\text{OEt}) \cdot \text{CN}$, which, on hydrolysis, was converted into the acid $\text{C}_6\text{H}_5 \cdot \text{CMe}(\text{OEt}) \cdot \text{CO}_2\text{H}$; the latter, with concentrated hydrochloric acid, gave atropic acid (III), from which tropic acid was prepared in the manner described above.

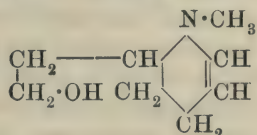
The determination of the constitution of tropine, the other decomposition product of atropine, was a much more difficult task, which Ladenburg attacked with great vigour. He found that when tropine, $\text{C}_8\text{H}_{15}\text{ON}$, was heated with concentrated hydrochloric acid, it was converted into tropidine, $\text{C}_8\text{H}_{13}\text{N}$ (*Ber.*, 1879, **12**, 944; 1880, **13**, 252); when heated with hydriodic acid, it gave an iodide, $\text{C}_8\text{H}_{15}\text{NI}_2$ (*Ber.*, 1881, **14**, 227), which, on reduction with zinc and hydrochloric acid, yielded hydrotropidine, $\text{C}_8\text{H}_{15}\text{N}$ (*Ber.*, 1883, **16**, 1408). When distilled with soda-lime, tropine gave methylamine, trimethylamine, hydrogen, and a hydrocarbon which was suspected to be valerylene, but its nature was not established (*Ber.*, 1881, **14**, 227).

As these results seemed to indicate that tropine was a derivative of a reduced pyridine or an oxidised piperidine nucleus, he prepared various alkylpiperidine derivatives, among others, *N*-propyl- and *N*-isopropyl-piperidine, and tried to convert these compounds by oxidation and other means into a base, which might prove to be identical with tropine or tropidine (*Ber.*, 1881, **14**, 1342). These experiments having failed, and the degradation of tropine by distillation with soda-lime having given such poor results, he next applied to this base a method which had been recently discovered by Hofmann, the now well-known process of exhaustive methylation.

From tropine and methyl iodide he obtained an iodide of methyl-tropine, $\text{C}_9\text{H}_{17}\text{ON}$, and found that this base was decomposed by

potassium hydroxide, giving dimethylamine (*Ber.*, 1881, **14**, 2126). Methyltropine, on further methylation, gave dimethyltropine iodide, from which by distillation, he obtained trimethylamine, an oil, $C_7H_{10}O$, which he named *tropilene*, and a hydrocarbon of the composition C_7H_8 , which he called *tropilidene* (*Ber.*, 1881, **14**, 2403); this hydrocarbon seemed to be identical with that which he had previously obtained from tropine.

The composition and properties of tropilene led Ladenburg to conclude that this compound was related to suberone; he oxidised it with nitric acid, and found that it gave an acid which was probably normal adipic acid (*Ber.*, 1882, **15**, 1028). At the same time he discovered another very important fact, namely, that tropidine hydrobromide, heated with bromine at $170-180^\circ$, gave ethylene dibromide and dibromomethylpyridine; with excess of bromine it gave ethylene dibromide and dibromopyridine (*Ber.*, 1882, **15**, 1140). From all these observations he concluded that tropine was probably a methylpiperidine or methylpyridine derivative of the following constitution (*Ber.*, 1882, **15**, 1028):



While these experiments were in progress he also examined several of the other mydriatic drugs; in the course of this work he showed that duboisine and daturine were probably identical with hyoscyamine, that belladonine probably contained atropine, and that hyoscyamine and atropine were very closely related, so closely, in fact, that atropine could be synthesised from the decomposition products of hyoscyamine.

About 1882, Ladenburg's direct study of these mydriatic alkaloids gave place to his synthetic work on piperidine and pyridine derivatives. The main object of these researches was, no doubt, the synthesis of tropine, since he thought that this base was related to pyridine in the manner shown above.

The first important step in these synthetical experiments was the discovery that pentamethylenediamine could be obtained by the reduction of trimethylene dicyanide with zinc and hydrochloric acid (*Ber.*, 1883, **16**, 1149). This base, heated with sodium hydroxide, gave a compound, $C_5H_{11}N$, which seemed to be piperidine, and the identity of the synthetic base with that obtained from pepper was fully established by Ladenburg and Roth (*Ber.*, 1884, **17**, 513). As the yield of pentamethylenediamine in the above process was very unsatisfactory, Ladenburg devised a better

method for the preparation of the base, which consisted in reducing the dicyanide with sodium and alcohol (*Ber.*, 1885, **18**, 2956); he also showed that the hydrochloride of the diamine was converted into piperidine and ammonium chloride when it was distilled; as this change was evidently no far-reaching decomposition, the synthesis of piperidine in this way established the constitutional formula at that time assigned to that base.

While this synthesis of piperidine was in progress, he studied the behaviour of pyridine ethiodide at high temperatures (*Ber.*, 1883, **16**, 1410), and found that it gave ethylpyridine hydriodide when it was heated, by intramolecular change, just as the *N*-substituted anilines were known to give homologues of that base (Hofmann). He proved that the product contained γ -ethylpyridine by oxidising a fraction of it to isonicotinic acid (*Ber.*, 1883, **16**, 2059), and also showed later (*Ber.*, 1885, **18**, 2961) that α -ethylpyridine and $\alpha\gamma$ -diethylpyridine were also produced, together with the γ -ethyl derivative, when pyridine ethiodide was heated.

It was now possible to obtain derivatives of pyridine from that base itself; in order to convert these compounds into the corresponding piperidine derivatives, Ladenburg investigated a method described by König for the reduction of pyridine to piperidine with zinc and hydrochloric acid, but he was unable to obtain any piperidine. He next tried reduction with sodium and alcohol, a process used by Wischnegradsky, and by a suitable improvement of this method, he was able to reduce coal tar picoline almost completely. In this way he obtained α -methylpiperidine, mixed with the β -compound, the first homologues of piperidine, excluding the *N*-derivatives, which had been prepared (*Ber.*, 1884, **17**, 388). He also reduced his γ -ethylpyridine to the piperidine derivative, and found that the latter had an odour of coniine.

This observation and the results of Hofmann's work, which had shown that coniine was in all probability α -propylpiperidine, led Ladenburg to attempt the synthesis of the last-named compound. With this end in view, he heated pyridine propiodide, and obtained a mixture of bases; one of these compounds gave, on oxidation, pyridine- γ -carboxylic acid, and seemed to be γ -propylpyridine; the other could not be obtained in a state of purity. The pure and the impure isomerides were separately reduced to piperidine derivatives; these compounds resembled coniine, but neither was identical with the latter. Immediately afterwards, with Schrade, he prepared α - and γ -isopropylpyridine in a similar manner from pyridine isopropiodide (*Ber.*, 1884, **17**, 1121). As these two compounds, like the supposed propyl derivatives, could not be completely separated by distillation, he converted the crude bases into the

corresponding piperidine derivatives by reduction with sodium and alcohol (*Ber.*, 1884, **17**, 1676), and then purified the latter with the aid of their platinichlorides.

The α -isopropylpiperidine thus obtained in a pure condition was carefully compared with coniine, and found to be remarkably similar to that base in all its properties, including its physiological action; the observed differences might be due merely to the optical inactivity of the synthetical base.

It was then found (*Ber.*, 1885, **18**, 1587) that the α - and γ -isopropylpyridines and also the supposed corresponding propyl derivatives could be completely purified with the aid of their platinichlorides; in each case the base of lower boiling point gave on oxidation picolinic acid, and was therefore the α -derivative, whilst the isomeride gave isonicotinic acid, and was therefore the γ -derivative.

The pure α -pyridine bases (propyl and isopropyl) were carefully compared with conyryne, which Hofmann had obtained by heating coniine hydrochloride with zinc dust, and had shown to be either α -propyl or α -isopropylpyridine. They both differed from conyryne. Therefore, either the difference was merely due to stereoisomerism, or else the two synthetical bases must both be isopropylpyridine. The latter alternative was proved to be the true one; when pyridine propiodide was heated in order to convert it into propylpyridine, the *n*-propyl was transformed into the isopropyl group.

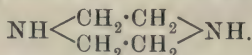
Since it had thus been proved that conyryne must be α -propylpyridine, Ladenburg attempted to prepare this base from pyridine allyl iodide, but obtained isopropylpyridine in place of the desired propyl compound (*Ber.*, 1885, **18**, 1587). Next he tried to condense picoline with paracetaldehyde in the presence of zinc chloride (*Ber.*, 1886, **19**, 439), a reaction which Jacobsen and Reimer had applied to obtain benzylidenequinaldine from quinaldine and benzaldehyde. In this way he obtained only very small quantities of an oily base, but the product had an odour of conyryne, and on analysis seemed to be allylpyridine. On reduction with sodium and alcohol, it gave a base having properties similar to those of coniine. These experiments were repeated with larger quantities of material (*Ber.*, 1886, **19**, 2578); 380 grams of picoline were treated in sealed tubes, and 45 grams of allylpyridine were obtained; the product was proved to be the α -derivative by oxidising it to picolinic acid, and was reduced to propylpiperidine; the latter was oxidised by Hofmann's method (*Ber.*, 1884, **17**, 825) to a base, which was found to be identical with conyryne. The synthetical propylpiperidine was finally converted into the acid tartrate, and the solution of the latter was seeded with a crystal of coniine acid tartrate; the crystal-

line deposit was decomposed with potassium hydroxide, and the liberated base was found to be dextrorotatory. The complete identity of the synthetical base with coniine, obtained from the hemlock, was then fully established; the alkaloid which had caused the death of the wisest of men was the first to succumb to the synthetic skill of the chemist!

This synthesis of coniine was accomplished in 1886, and for nearly twenty years afterwards Ladenburg continued his researches with undiminished activity. During this period he was occupied to a great extent with various issues arising out of his earlier work; it will therefore be more convenient to deal with the discoveries of this period under certain definite headings rather than to consider them in strict chronological sequence.

His studies of the diamines may be first considered (*Ber.*, 1886, **19**, 2585). He showed that his synthetical pentamethylenediamine was identical with cadaverine, a base isolated by Brieger from putrefying flesh. Tetramethylenediamine (*Ber.*, 1886, **19**, 780;

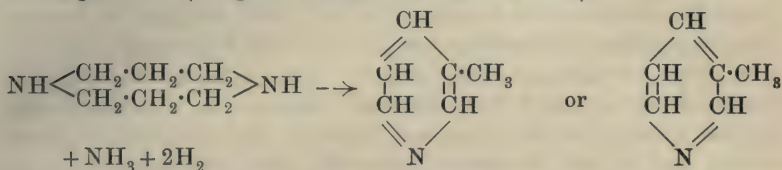
1887, **20**, 442) was converted into pyrrolidine, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{NH}$, by the same method as that by which piperidine had been obtained from pentamethylenediamine, and pyrrolidine was also synthesised by reducing succinimide with sodium and alcohol (*Ber.*, 1887, **20**, 2215). The action of heat on ethylenediamine hydrochloride resulted in the formation of a base (*Ber.*, 1888, **21**, 758; 1890, **23**, 3740; 1891, **24**, 2400), which is now well known as piperazine.



By the distillation of ethylenediamine hydrochloride with sodium acetate he obtained a base, lysidine, $\begin{array}{c} \text{CH}_2 \cdot \text{NH} \\ | \quad \diagup \\ \text{CH}_2 \text{---N} \end{array} \gg \text{C} \cdot \text{CH}_3$ (*Ber.*, 1894, **27**, 2952), identical with a compound prepared by Hofmann (*Ber.*, 1888, **21**, 2332) in an analogous manner. Lysidine, like piperazine, formed with uric acid a salt which was very readily soluble in water (*Ber.*, 1894, **27**, 2952), and clinical experiments, carried out at Ladenburg's suggestion, showed that a case of acute, and also one of chronic arthritis were both quickly cured by large doses of this base.

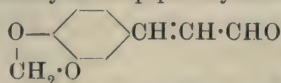
The action of heat on trimethylenediamine hydrochloride resulted, not only in the formation of trimethyleneimine, $\text{CH}_2 < \begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{NH}$, but also in the production of two picolines (*Ber.*, 1890, **23**, 2727); the production of these two pyridine derivatives was explained by assuming that the diamine first gave rise to a homologue of

piperazine, $\text{NH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{NH}$, which then decomposed with formation of ammonia and two molecules of hydrogen, the eight-membered ring suffering disruption, and passing into a mixture of two β -picolines (compare also *Ber.*, 1890, **23**, 2688):



His investigations on pyridine derivatives led him to consider the orientation of the pyridinecarboxylic acids, and he pointed out the important fact that when a pyridinedicarboxylic acid was heated, the α -carboxyl group was always the first to be eliminated (*Ber.*, 1885, **18**, 2967). He isolated lutidine (*Ber.*, 1885, **18**, 913) and γ -picoline (*Ber.*, 1888, **21**, 285) from coal tar, and reduced these compounds to the corresponding piperidine derivatives. He showed that α -methyl- and α -ethylpiperidine could be resolved into their optically active components (*Ber.*, 1886, **19**, 2584, 2975), and that picolinic acid (*Ber.*, 1891, **24**, 640), as well as nicotinic and isonicotinic acids (*Ber.*, 1892, **25**, 2768) could be reduced with sodium and alcohol to the corresponding piperidinecarboxylic acids. A summary of his work on pyridine and piperidine derivatives down to 1888 is given in the *Annalen*, 1888, **247**, 1.

The partial synthesis of piperine from piperidine and the chloride of piperic acid having been carried out by Rügheimer in the Kiel laboratory, the last link required to complete the chain was forged by Ladenburg and Scholtz (*Ber.*, 1894, **27**, 2958). Piperonal was condensed with acetaldehyde to piperonylacrolein,



and the latter, with the aid of sodium acetate and acetic anhydride, was converted into an acid,



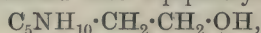
identical with the piperic acid obtained from piperine.

His analytical and synthetical experiments on tropine, which had been interrupted by his work on coniine, were continued intermittently down to 1902. Hydrotropidine hydrochloride, when heated, gave methyl chloride and a base, $\text{C}_7\text{H}_{13}\text{N}$, which he named norhydrotropidine; the hydrochloride of the latter, under similar conditions, gave α -ethylpyridine, together with a small quantity of

a hydrocarbon (*Ber.*, 1887, **20**, 1647). He also showed that tropidine was converted into tropine by treatment with hydrobromic acid (*Ber.*, 1890, **23**, 1780, 2225; 1902, **35**, 1159, 2295).

The resolution of tropic acid into its optically active components (Ladenburg and Hundt, *Ber.*, 1889, **22**, 2590) led to the preparation of optically active atropines, which were obtained by evaporating the active acids with a solution of tropine hydrochloride.

A large proportion of his work on tropine at about this time consisted of repeated but fruitless attempts to synthesise this elusive base. For this purpose, starting from piperidine derivatives, and using Hofmann's method (*Ber.*, 1885, **18**, 111), he prepared various tetrahydropyridine derivatives (*Ber.*, 1887, **20**, 1645) which he thought were related to tropine. He also prepared α -picolylalkine, $C_5NH_4 \cdot CH_2 \cdot CH_2 \cdot OH$, by the condensation of picoline and formaldehyde; this compound on distillation gave vinylpyridine, $C_5NH_4 \cdot C_2H_3$, which had a strong odour of conyryne, and on reduction was converted into α -pipecolylalkine,



a base nearly related to tropine in composition and properties (*Ber.*, 1889, **22**, 2583). These synthetical experiments were, of course, predestined to fail, because they were founded on an erroneous view of the constitution of tropine; this fact, however, does not detract from the value of Ladenburg's positive results, which threw so much light on the nature of tropine and formed so excellent a foundation for the brilliant synthesis ultimately accomplished by Willstätter.

In another long series of papers, published between 1893 and 1906, Ladenburg follows up the discovery of a base which he regarded as a stereoisomeride of coniine. He found (*Ber.*, 1893, **26**, 854) that when coniine hydrochloride was distilled with a relatively small quantity of zinc dust, in addition to conyryne and unchanged coniine, it gave an optically active propylpiperidine, which differed from coniine in specific rotation and in certain other respects. He accounted for the existence of this base, which he named *isoconiine*, by assuming that the arrangement of the atoms or groups around the nitrogen atom was an asymmetric one, or, at any rate, that such an arrangement could modify the optical activity conditioned by the asymmetric carbon group (*Ber.*, 1896, **29**, 2718). By a method similar to that used in the conversion of coniine into *isoconiine*, he prepared from *d*-pipecoline an isomeric base, *isopipecoline* (*Ber.*, 1894, **27**, 853), and by heating *l*-stilbazoline (*Ber.*, 1903, **36**, 3694), a compound obtained by resolving the reduction product of stilbazole, $C_5NH_4 \cdot CH:CH \cdot C_6H_5$, he prepared *isostilbazoline* (*Ber.*, 1904, **37**, 3688). He made many

experiments to try and prove that these optically active *iso*-bases were definite compounds, and not mere mixtures in unequal proportions of the *d*- and *l*-isomerides (*Ber.*, 1895, **28**, 163; 1896, **29**, 2706; 1897, **30**, 485), and he also attempted unsuccessfully to obtain other nitrogenous compounds showing isomerism of the same nature (*Ber.*, 1896, **29**, 2710; 1897, **30**, 1582). In his last paper on this subject (*Ber.*, 1906, **39**, 2486), although he maintained the existence of *isoconiine*, the facts which he himself had established were so difficult to reconcile with his views that he was obliged to conclude that his own synthetical coniine was in reality the *iso*-base, and that the latter was only converted into natural coniine when it was strongly heated. An impartial verdict on this branch of Ladenburg's work may perhaps be implied by the statement that he is not the only chemist who has unsuccessfully devoted time and effort to prove the existence of asymmetry in tervalent nitrogen compounds.

In the course of his experiments on the resolution of piperidine derivatives and during his study of the active bases, Ladenburg made some important contributions to our knowledge of asymmetric compounds. He was the first to show that *dl*-bases could be resolved by the method discovered by Pasteur, and used by the latter for the resolution of *dl*-acids. He also showed that a lowering of temperature occurred when *d*- and *l*-coniine were mixed (*Ber.*, 1895, **28**, 163), whereas no change in temperature was observed in the case of certain other liquids of similar character, having the same specific gravity (*Ber.*, 1895, **28**, 1991). From these facts he argued that *d*- and *l*-coniine united to form a racemic liquid.

A general method for distinguishing solid racemic compounds from *dl*-mixtures was also put forward (*Ber.*, 1894, **27**, 3065), but as the result of adverse criticism, this method was modified as follows (*Ber.*, 1899, **32**, 864): "To decide whether an inactive, resolvable substance is a racemic compound or a mixture of active components, the solubility of the substance is determined with and without the addition of a small quantity of one of the active components (at the same temperature and in the same solvent). If the solubilities are different, the substance is racemic; if the same, it is an enantiomorphous mixture.

During some experiments on the resolution of β -pipecoline with the aid of tartaric acid, he found that when crystallisation occurred at about 100° the experiments failed, whereas at the ordinary temperature the *dl*-base was resolved (*Ber.*, 1894, **27**, 75); also, that the resolution of pyrotartaric acid (methylsuccinic acid) could be accomplished with the aid of strychnine (*Ber.*, 1895, **28**, 1170), but not with quinine. These results led him to conclude that the

dl-base formed with the *d*-acid and the *dl*-acid formed with the *l*-base a salt, one part of the molecule of which was racemic, the other part optically active. To such salts he applied the term half or partly racemic, which had been previously used by E. Fischer (*Ber.*, 1894, **27**, 3225) to denote mixtures, or compounds, of two optically active components which were similar but not enantiomorphously related.

The study of these partly racemic salts was described in numerous papers (*Ber.*, 1898, **31**, 524, 937, 1969; 1899, **32**, 50; 1903, **36**, 1649; 1907, **40**, 2279; 1908, **41**, 966), and a summary of the results was given in the *Annalen* (**364**, 227) in 1909. His experiments were chiefly directed towards obtaining evidence that the two types of partly racemic salts, namely, *dAlB*, *lAlB*, and *dAdB*, were not merely mixtures, but were definite compounds. For this purpose he compared the properties of partly racemic strychnine *dl*-tartrate, *dAlB*, *lAlB*, with those of the *dAlB* and *lAlB* salts of strychnine and tartaric acid. He showed that the three compounds differed as regards the hydration of their crystals: also in solubility, specific gravity, specific rotation, and so on; and that the qualitative data could not be reconciled with the view that the partly racemic salt was a mere mixture of the *dAlB* and *lAlB* components. He also proved that partly racemic strychnine tartrate and brucine hydrogen tartrate had a transition temperature above which they underwent resolution. On the other hand, *dl*-pipecoline *d*-tartrate, which was deposited as a partly racemic salt at high temperatures, had a transition temperature below which it was resolved; *dl*-tetrahydroquinaldine hydrogen *d*-tartrate behaved in a similar manner. From all these results, Ladenburg concluded that the formation of partly racemic salts was a very general phenomenon; further, that the formation of such salts was strong evidence in support of the view that racemic compounds could exist in a dissolved state.

In 1898 he was able to break new ground with the aid of an apparatus for the liquefaction of air. He described various lecture experiments suitable for the illustration of low temperature effects (*Ber.*, 1898, **31**, 1968), and also determined the specific gravities of liquid air and other liquefied gases (*Ber.*, 1899, **32**, 46), as well as their boiling points (*Ber.*, 1899, **32**, 1818). He liquefied ozonised oxygen (*Ber.*, 1898, **31**, 2508), purified the ozone by fractional evaporation, and determined the density of this purified material with the aid of Schilling's apparatus; the purity of the samples, that is to say, the proportion of ozone which they contained, was checked by a titration of the iodine liberated from potassium

iodide by a known quantity of the gas. The density was thus found to be 1.456 ($O=1$).

In other papers (*Ber.*, 1898, **31**, 2830; 1900, **33**, 2283) dealing with this matter, he replied to objections which had been raised to his method on the grounds that he had used the formula O_3 for ozone in calculating the proportion of this gas in his samples. He then worked out the details of a process for estimating the ozone in a weighed quantity of ozonised oxygen with the aid of turpentine (*Ber.*, 1901, **34**, 631); he was thus able to determine the density of ozone without the use of potassium iodide. Later still (*Ber.*, 1901, **34**, 1184) he showed that the usual method for the estimation of ozone, with the aid of an acidified solution of potassium iodide, gave results which were 50 per cent. higher than the true values, but that correct estimations could be made if the gas were first absorbed in neutral solutions of potassium iodide, which were then acidified before titration.

The interesting question as to the relative positions of iodine and tellurium in the periodic system led Ladenburg to take up the study of the first-named element. He showed (*Ber.*, 1902, **35**, 1256) that silver iodide could be readily freed from silver chloride by repeated extraction with a concentrated solution of ammonium hydroxide until the solubility of the iodide became constant; he reduced the pure iodide with zinc and sulphuric acid, decomposed the zinc iodide which was thus formed with nitrous acid, and distilled the well-washed precipitated iodine in steam. He then determined the melting point, boiling point, and specific gravity of the pure halogen.

Shortly afterwards (*Ber.*, 1902, **35**, 2275) he made a series of determinations of the atomic weight of iodine, based on the conversion of silver iodide into silver chloride and a knowledge of the atomic weights of silver and chlorine. From the results of this work, he found the atomic weight, $I=126.96$, a value considerably higher than that (126.85) obtained by Stas, but which approximates very closely to that (126.92) which is given in the last report of the International Committee on Atomic Weights.

A list of Ladenburg's papers is given in the *Berichte* (1912, **45**, 3636).

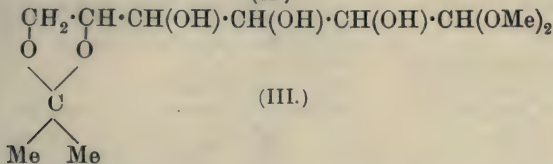
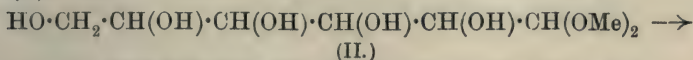
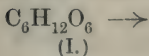
CCIII.—*The Mechanism of the Condensation of Glucose with Acetone.*

By JAMES LESLIE AULD MACDONALD (Carnegie Scholar).

DURING the past five years the preparation of glucose-monoacetone and -diacetone has been carried out in this laboratory on twenty occasions, the process being modified in various ways (Irvine and Scott, this vol., p. 563). The yields obtained have been very irregular, and, what is more surprising, the amount of monoacetone derivative fluctuated in the most remarkable manner. The conclusion drawn is that the simplest possible explanation, namely, that the reaction consists of the simultaneous hydrolysis of glucose-dimethylacetal and condensation with the solvent acetone, is untenable. Such a process should result, in the first instance, in the formation of a glucosidic monoacetone derivative, followed by a second condensation with the ketone, the final product being entirely glucosediacetone. The following research was undertaken in the hope of tracing the mechanism of the reaction, so as to improve the working methods of preparing these derivatives and to throw light on their constitution, as they may play an important part in the future development of synthetical work in the sugar group.

As glucosemonoacetone possesses a glucosidic structure, the formation of the compound must of necessity involve a process of simultaneous hydrolysis and condensation, in which glucosedimethylacetal parts with the acetal grouping and reacts with the solvent ketone. A reaction of this kind does not account for the persistence of glucosemonoacetone however long the treatment with the ketone may be extended. This type of reaction is, moreover, uncommon in the sugar group, and does not take place to any appreciable extent with acyl derivatives of glucose; thus, α -penta-acetyl glucose, when dissolved in acetone containing the same percentage of hydrogen chloride as is necessary for the decomposition of glucose-dimethylacetal, readily lost the acyl groups at the temperature of the room, but no condensation with the solvent took place, and the main product consisted of glucose. An attempt was therefore made, starting from glucosedimethylacetal, to arrest the condensation at the earliest possible stage, and thus isolate the first product of the reaction. This was carried out as explained in the experimental part, and a product obtained, which, although too unstable to permit of analysis, possessed the reactions which would be char-

acteristic of a glucosedimethylacetalmonoacetone. The first stages of the reaction are therefore expressed in the following scheme:



Since glucosedimethylacetalmonoacetone is the main product of the initial stages of the condensation of acetone with glucose-dimethylacetal, a knowledge of its properties should furnish valuable evidence for establishing the mechanism of the formation of glucose-monoacetone and -diacetone.

A most significant property of the compound is that on further treatment with acid acetone it yields glucosediacetone, and it is probable that this is the main route by which the latter compound is formed when prepared by the usual method.

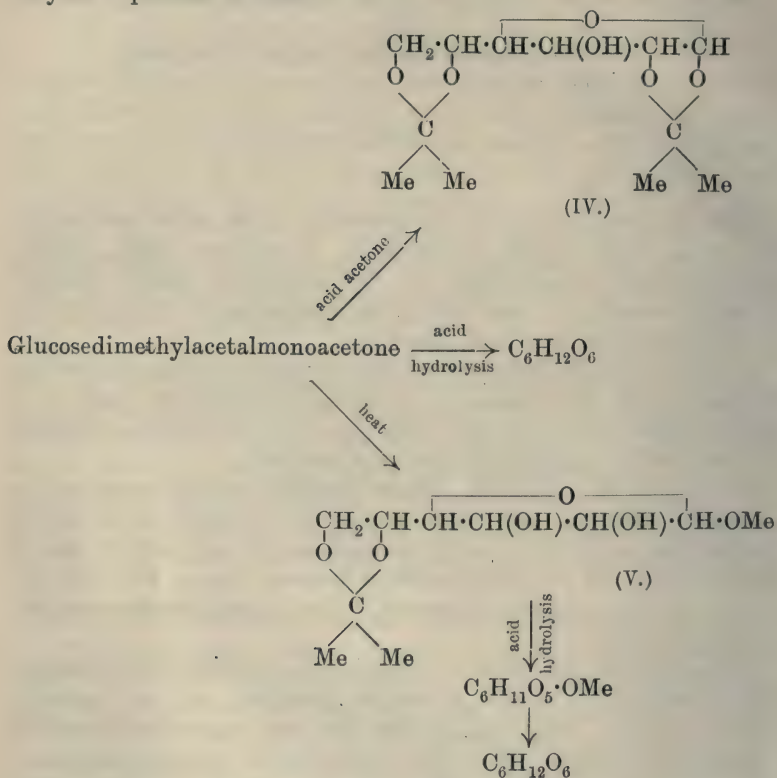
As might be expected, glucosedimethylacetalmonoacetone is extremely unstable, and when heated in a vacuum at as low a temperature as 20° it is readily decomposed, a molecule of methyl alcohol being lost by ring-formation between the α - and δ -carbon atoms, and the γ -oxidic compound,* methylglucosidemonoacetone, is thus produced.

In the light of the above explanation the product of this change should contain a stable glucosidic grouping and an unstable acetone residue. That such is the case was proved by carefully regulated hydrolysis. The crude glucosedimethylacetalmonoacetone was heated in a vacuum until constant in weight, and the syrup obtained hydrolysed with hydrochloric acid of a concentration insufficient to cause decomposition of methyl glucoside. In this way the acetone residue was removed without attacking the glucosidic position, and the final product, as indicated by the rotation value obtained, was an equilibrium mixture of α - and β -methyl glucosides. This result cannot be explained on any assumption other than the elimination of methyl alcohol from the acetal and the formation of methylglucosidemonoacetone (V).

* The nomenclature here adopted to express the position of substituent groups in the sugar molecule is the same as that used in this vol., p. 564.

It is perhaps necessary to point out that if the expression " γ -oxidic linking" is to be retained, the adoption of this system involves a certain amount of dubiety as the γ -linking connects the α - and δ -carbon atoms of the sugar.

Glucosedimethylacetalmonoacetone, like other acetone compounds, is highly sensitive to dilute acids, which remove the acetone residue and simultaneously hydrolyse the acetal grouping, the final product of the reaction being the parent hexose. These reactions may be expressed as follows:



Structure and Constitution of Intermediate Compounds.

As Irvine and his collaborators have already pointed out, the position taken up by an acetone residue when entering a sugar molecule, where the number of hydroxyl groups renders the formation of isomeric forms possible, depends largely on the relative stability of the rings thus produced. This stability is influenced by two factors, namely, (a) the number of atoms forming the ring, and (b) the position of the hydroxyl groups relative to the plane of the γ -oxidic ring of the sugar.

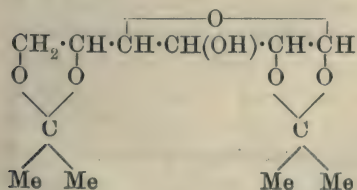
Since glucosedimethylacetalmonoacetone readily forms a glucoside it follows that the acetone residue cannot be linked to the δ -carbon atom. Methylglucosidemonoacetone must therefore have two free

hydroxyl groups, and the position of these may be established by methylation and hydrolysis of the resulting compound. This was carried out, and a dimethyl methylglucoside and finally a dimethylglucose were obtained. The general reactions, solubilities, and rotation values of the dimethylglucose thus isolated corresponded with those quoted by Irvine and Scott (this vol., p. 575) for $\beta\gamma$ -dimethyl glucose. The optical values are compared below:

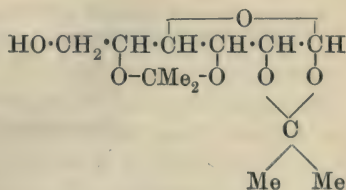
Solvent.	$[\alpha]_D^{20}$ for dimethylglucose obtained from dimethyl methylglucosidemonoacetone.	$[\alpha]_D^{20}$ for $\beta\gamma$ -dimethylglucose (Irvine and Scott).
Water.....	+65.3°	+64.4°
Methyl alcohol ...	+57.2	+58.1 *
Ethyl alcohol ...	+50.0	+49.4

* New determination.

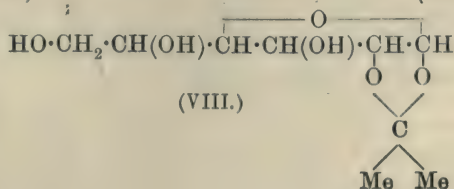
Although the methylated sugar could not on this occasion be obtained crystalline, the resemblance is sufficiently striking to warrant the conclusion that the compound is $\beta\gamma$ -dimethylglucose. From this it follows that the acetone residue in methyl glucosidemonoacetone and glucosediethylacetalmonoacetone is linked to carbon atoms ϵ and ζ . Now, since glucosediacetone is obtained by further condensation of acetone with glucosediethylacetalmonoacetone, it follows that the acetone residue not attached to the reducing group in this compound is in the $\epsilon\zeta$ -position. This is not in agreement with the constitution assigned to glucosediacetone by Irvine and Scott (this vol., p. 564), although it was there pointed out that the evidence on which the suggested constitution is based was capable of a different interpretation. Glucosediacetone formed in the manner now described must have the following structure (VI), provided that the glucosidic acetone residue forms a five-membered ring. Formula (VII) represents the alternative constitution advanced by Irvine and Scott:



(VI.)



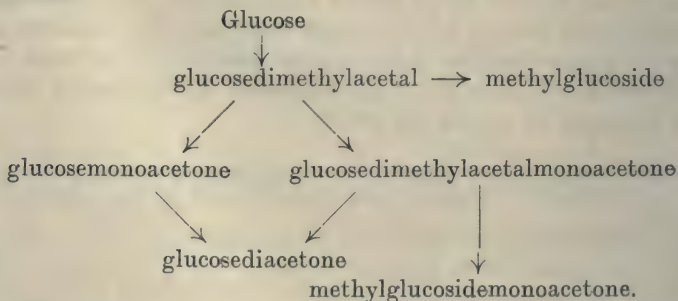
(VII.)



(VIII.)

If the above reasoning be accepted the monomethyl glucose described by Irvine and Scott must have the alkyl group in the γ -position, and this conclusion harmonises with all the available evidence regarding the structure of this compound. It may be mentioned here that an extended investigation of the sugar has now been commenced in this laboratory. It is evident, however, that glucosediacetone may also be formed by a different route. When acid acetone is brought into contact with glucosedimethylacetal the first reaction may be the hydrolysis of the acetal grouping and the entry of a molecule of acetone in the $\alpha\beta$ -position producing the glucosemonoacetone isolated by Fischer (*Ber.*, 1895, **28**, 2496), formula (VIII), which in turn condenses with a second molecule of acetone to form the di-derivative. The second molecule of acetone may be attached in three alternative ways; the linking may be γ and ζ , γ and ϵ , or ϵ and ζ . The first possibility may be rejected on stereochemical grounds, since a seven-membered ring is involved. Comparing the two remaining alternatives, it will be seen that formula (II) requires the formation of a six-membered ring having a *trans*-configuration in respect of the γ -oxidic ring, a condition involving severe molecular strain. Formula (I) is therefore the more probable, and the fact that only one glucosediacetone has been isolated, although not conclusive, tends to strengthen this view.

The series of probable changes which take place in the formation of acetone derivatives of glucose are thus expressed in the following scheme:



A review of the whole sequence of changes indicates in a striking manner the complexities introduced into the reactions of the sugars when the latter are converted, even temporarily, into straight-chain derivatives of an acetal nature.

EXPERIMENTAL.

Glucosedimethylacetal.

The conditions laid down by Fischer (*loc. cit.*) were, in essentials, followed in the preparation of this compound. Inasmuch as the preparation was carried out on a much larger scale than that employed by Fischer, it was found convenient, in the first place, to make a solution of dry powdered glucose (90 grams) by boiling the sugar with pure dry methyl alcohol, and, after cooling, to add the requisite amount of hydrogen chloride dissolved in methyl alcohol so as to make the final volume 1600 c.c. and the acid content 1.5 per cent. After remaining at the temperature of the room for sixty hours the acid was removed by shaking first with dry powdered barium carbonate and finally with silver carbonate. After shaking with freshly ignited animal charcoal the solvent alcohol was removed at 35°/15 mm., a Winchester bottle being used as a distilling flask. The syrupy residue was well shaken with 300 c.c. of dry acetone, which was subsequently removed in a vacuum. In this way a clear, colourless syrup was obtained lining the sides and bottom of the bottle, these conditions being extremely well adapted for the subsequent treatment with acetone.

Glucosedimethylacetalmonoacetone.

Five hundred c.c. of dry acetone containing 0.5 per cent. of hydrogen chloride were added to the crude glucosedimethylacetal, and the contents of the bottle were subjected to alternate shaking and heating on the water-bath at 35° for three and a-quarter hours. To aid the incorporation of the syrup with the acetone some chips of porous porcelain were added. The acetone liquor was poured off, and immediately neutralised with barium carbonate, followed by treatment with silver carbonate and charcoal. The undissolved syrup remaining in the bottle was given a further treatment with acid acetone for the same period. A third treatment yielded a negligible amount of product. Extracts 1 and 2 were mixed and dried over anhydrous sodium carbonate. The solution was then concentrated to about one-third of the volume over fresh carbonate on the water-bath, filtered, and concentrated further in a vacuum at a low temperature. When the liquor had become slightly syrupy the concentration was stopped, and a large volume of dry light petroleum added. This precipitated a transparent, colourless, mobile syrup, from which the mother liquor was poured away, and fresh quantities of light petroleum were added from time to time. The deposition of the syrupy product extended over several weeks.

The product, which amounted to 25 per cent. of the glucose used, was extremely soluble in water, cold acetone, or warm ethyl acetate.

The reactions of the compound were essentially the same as those of glucosdimethylacetal, but the increased solubility indicated that condensation with acetone had proceeded. All attempts to confirm the idea that the syrup consisted of glucosdimethylacetalmonoacetone by means of analyses were fruitless. When dried in a high vacuum at the minimum possible temperature the combustion results obtained corresponded with those required for methylglucosidemonoacetone, indicating that a molecule of methyl alcohol had been removed during the drying process.

Hydrolysis of Glucosdimethylacetalmonoacetone.

Hydrolysis of glucosdimethylacetalmonoacetone syrup, which had been heated in a vacuum at 30° until constant in weight, was carried out under conditions which do not affect methylglucoside.

A 2.5 per cent. solution of the syrup was prepared in 50 per cent. ethyl alcohol containing 0.5 per cent. of hydrogen chloride, and the solution examined polarimetrically in a jacketed tube, which was maintained at 30°. Under these conditions hydrolysis was complete in eighty hours. Some of the readings obtained are appended:

Time in hours.	α^{30° .	$[\alpha]_D^{30^\circ}$.
0	-0.74°	-15.10°
1	-0.79	-16.12
3	-0.62	-12.65
6	-0.29	-5.29
9	-0.04	-0.82
19	+0.60	+12.24
26	+1.00	+20.40
30	+1.20	+24.49
40	+1.49	+30.40
63	+1.87	+38.16
80	+1.89	+38.57

$l=2$.

Methylglucoside- ϵ -monoacetone.

The crude glucosdimethylacetalmonoacetone described above was dried at 22°/12 mm. until constant in weight. A colourless syrup then remained, which could not be obtained crystalline.

Found: C=51.19; H=7.71; OMe=11.2.

C₉H₁₅O₅·OMe requires C=51.25; H=7.69; OMe=13.2 per cent.

The following rotation values were observed:

Solvent.	c .	l .	α^{20° .	$[\alpha]_D^{20^\circ}$.
Methyl alcohol	4.451	1	-0.52°	-11.68°
Ethyl alcohol	4.110	1	-0.47	-11.43

The compound, which was practically devoid of action on Fehling's solution, was readily soluble in water, methyl and ethyl alcohol, acetone, ethyl acetate, or ether, but only moderately so in methyl iodide. When heated in a vacuum at 60° for some time it was partly hydrolysed, and gave an insoluble residue when extracted with dry ether. The reactions and solubilities of this residual product agreed with those of methyl glucoside, thus indicating that the acetone residue had been removed.

βγ-Dimethyl Methylglucoside-εζ-monoacetone.

The alkylation of the methylglucosidemonoacetone was carried out by the silver oxide method in the usual way. Three times the theoretical quantity of alkylating mixture was used, and, owing to the sparing solubility of the unalkylated compound in methyl iodide, a few c.c. of acetone had also to be added in the first methylation. To ensure complete alkylation two further treatments were given. On working up the final product in the usual manner a syrup (b. p. 142—143°/12 mm.) was obtained, having no action on Fehling's solution. The yield was slightly less than the weight of unalkylated material used.

Found: C=54·53; H=8·45; OMe=32·2.

C₉H₁₃O₃(OMe)₃ requires C=54·96; H=8·40; OMe=35·5 per cent.

Solvent.	c.	l.	α^{20° .	$[\alpha]_D^{20^\circ}$.
Methyl alcohol	6·11	1	-1·16°	-19·00°
80 per cent. ethyl alcohol	10·0	2	-2·98	-15·00

βγ-Dimethyl Methylglucoside.

A 10 per cent. solution of dimethyl methylglucosidemonoacetone in 80 per cent. alcohol containing 0·5 per cent. of hydrogen chloride was heated in boiling water for twelve hours, during which time the rotation altered from lævo to dextro and became constant. After neutralisation with silver carbonate the solvent was removed in a vacuum, and the resulting syrup dissolved in dry acetone. This solution was dried over magnesium sulphate, the solvent evaporated, and the residue extracted repeatedly with dry ether. After removal of the solvent in a vacuum an attempt was made to distil the product; a fraction almost without action on Fehling's solution and showing $[\alpha]_D^{20} + 15·28^\circ$ in methyl alcohol was thus obtained. Fractions of higher boiling point were more strongly dextro-rotatory, the maximum optical value recorded being +51·1°.

Found: C=48·05; H=7·87; OMe=40·3.

C₆H₉O₃(OMe)₃ requires C=48·65; H=8·11; OMe=41·9 per cent.

β -Dimethyl Glucose.

Complete hydrolysis of the glucoside described above was readily effected by heating an 8 per cent. solution of the compound in 80 per cent. alcohol containing 8 per cent. of hydrogen chloride at 90° for forty-five minutes. After neutralisation and removal of the solvent in a vacuum a syrup remained, which failed to crystallise, although attempts to affect this were continued throughout several months. (Found, C=45·99; H=7·59; OMe=30·2. $C_6H_{10}O_4(OMe)_2$ requires C=46·15; H=7·69; OMe=29·8 per cent.)

Solvent.	c.	l.	α^{20° .	$[\alpha]_D^{20^\circ}$.
Water... ..	1·056	2	+1·38°	+65·3°
Methyl alcohol ...	1·26	1	0·72	57·2
Ethyl alcohol ...	1·647	2	1·67	50·0

I take this opportunity of expressing my thanks to Professor J. C. Irvine for his valuable help and advice, which was at all times at my disposal during the course of this work, and also to the Carnegie Trust for a grant which partly defrayed the expenses of the research.

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UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS.

CCIV.—*The Solubilities of Alkali Haloids in Methyl, Ethyl, Propyl, and isoAmyl Alcohols.*

By WILLIAM ERNEST STEPHEN TURNER and CRELLYN
COLGRAVE BISSETT.

THE particular salts included in the scope of this investigation are lithium chloride and iodide, sodium chloride and iodide, potassium chloride, bromide and iodide, and rubidium chloride, of which we required information as to their solubility in connexion with other physical measurements in progress. The solubilities in water of all the salts mentioned had previously been measured, thus making possible a comparison with the solvent action of the alcohols, and a few measurements in the alcohols, to be referred to later, had also been carried out by various investigators.

The work detailed in this paper falls into three sections, namely, (1) the determination of the compounds formed between the alcohol and the salt at the temperature of the solubility measurements;

(2) the construction of the solubility curve of lithium chloride in ethyl alcohol for the temperature range 0—60°; and (3) the comparison of the solubilities of the salts at a common temperature of 25°.

The salts, initially the best commercially obtainable, were subjected to purification until analysis proved them to be pure. Rubidium chloride was prepared from a mixture of the bromide and iodide by the action of moist silver oxide and subsequent neutralisation of the base.

Some initial difficulty was experienced in obtaining the lithium salts, especially the iodide, quite free from water, but this was overcome finally by electrical heating in a vacuum, using the apparatus already described by us (P., 1913, **29**, 233).

The alcohols were thoroughly desiccated, the methyl and ethyl by lime, the propyl and *iso*amyl alcohols by anhydrous copper sulphate, and subsequently fractionated, most of the fractions being collected over a range of less than 0.1°.

Compounds of the Alkali Haloids with Alcohols.

As soon as the solubility measurements had been completed, the composition of the solid phase was determined in each case in the following manner. The solid was rapidly collected, removed to a porous porcelain tile, and placed in a desiccator containing a quantity of the pure solvent. This desiccator was in turn placed in the thermostat at the same temperature as that at which the solubility was determined, and the salt allowed to dry under these conditions. When ready for analysis the halogen content of a weighed portion was determined by the use of standard silver and potassium thiocyanate solutions.

Lithium Chloride and Methyl Alcohol.—Simon (*J. pr. Chem.*, 1879, [ii], **20**, 371) described a compound of the composition $\text{LiCl} \cdot 3\text{CH}_3\text{O}$, obtained by cooling a saturated solution of the salt to a temperature of -16° to -18°. This compound he speaks of as melting when its temperature is raised to that maintained in the laboratory. We found that the solid phase at 25° consists of the anhydrous salt.

Lithium Chloride and Ethyl Alcohol.—At 25° the solid phase was in this case also found to consist of the anhydrous salt. Simon obtained transparent, prismatic crystals of the composition $\text{LiCl} \cdot 4\text{C}_2\text{H}_5\text{O}$ by cooling a solution in a freezing mixture. Such a degree of cooling is unnecessary, for we found that the solution saturated at 25° gave a crystalline deposit at the laboratory temperature of about 14—15°. Determinations were accordingly made at a series of temperatures between 0° and 17.1°. The

percentages of lithium chloride found in the compound were, at 0°, 18.73; at 17.1°, 18.48; the calculated value for $\text{LiCl} \cdot 4\text{C}_2\text{H}_6\text{O}$ is 18.71. The transition point:



was found to lie at 17.4° (see below).

Lithium Iodide and Propyl Alcohol.—The solid phase at 25° crystallised in flat plates of a very deliquescent character, and analysis proved it to contain 35.52 per cent. of lithium iodide. For $\text{LiI} \cdot 4\text{C}_3\text{H}_7\text{O}$, which is obviously the composition of the compound, the calculated amount of lithium iodide is 35.78 per cent.

Sodium Iodide and Methyl Alcohol.—At 25° the solid phase was composed of the anhydrous salt, but when cooled to a temperature of 15–16° the liquid became packed with a mass of needle-shaped crystals, which were found to contain 61.96 per cent. of sodium iodide, whilst the calculated percentage for $\text{NaI} \cdot 3\text{CH}_3\text{O}$ is 60.95. The crystals rapidly effloresce when exposed to air, this fact readily accounting for the somewhat high analytical result.

No other compounds were discovered under the working conditions, although considerable heat was disengaged by the lithium salts and sodium iodide on solution in the various alcohols.

*The Solubility Curve of Lithium Chloride in Ethyl Alcohol.**

A series of measurements of the solubility of lithium chloride in ethyl alcohol was made in the following manner. A Beckmann freezing-point tube was fitted with an air-tight mercury cup-stirrer, of the type described by Findlay ("Practical Physical Chemistry," p. 238), the stem of the stirrer being hollow to permit of the removal of solution by means of a pipette of diameter slightly smaller than the stirrer, whilst the side-tube of the freezing-point tube was connected with U-tubes containing calcium chloride. Excess of solid with the alcohol were placed in the tube, usually

* After the preparation of this paper for publication we found that Lemoine (*Compt. rend.*, 1897, 125, 603) had made three determinations of the solubility of lithium chloride in methyl alcohol and six in ethyl alcohol. None of his results agrees with ours, and on the face of them, the measurements in ethyl alcohol challenge adverse criticism. Lemoine quotes Simon as proving the existence of the compounds $2\text{LiCl} \cdot 3\text{CH}_3\text{O}$ and $\text{LiCl} \cdot 2\text{C}_2\text{H}_5\text{O}$, whereas Simon himself gives them as $\text{LiCl} \cdot 3\text{CH}_3\text{O}$ and $\text{LiCl} \cdot 4\text{C}_2\text{H}_5\text{O}$, and our work confirms the existence of the latter substance. Lemoine states that his own analysis confirms the composition as $\text{LiCl} \cdot 2\text{C}_2\text{H}_5\text{O}$. No indication of the solubility method is given, and no determination of the solid phase in contact with the solution made, nor is the temperature given at which the presumed $\text{LiCl} \cdot 2\text{C}_2\text{H}_5\text{O}$ exists. The values given by Lemoine for solutions in ethyl alcohol are: at 1.6°, 16.28; 5.7°, 16.28; 13°, 14.94; 25°, 15.28; 40.6°, 17.65; 62.6°, 21.96 grams of salt per 100 grams of solvent. It is not easy to construct a curve based on these numbers.

in the form of a mixture of the nearly saturated solution with the excess of the solid phase stable at the temperature of measurement, the mixture being prepared in a tightly-stoppered bottle. The temperature variation of the thermostat used did not exceed 0.05° , except at 60° , where it reached 0.2° , but at this temperature the rate of change of solubility is very small. After vigorous stirring of the mixture for three or four hours, samples of the solution, usually between 1 and 2 grams in weight, were withdrawn by a pipette provided with a tightly packed plug of cotton-wool and an indiarubber clip, which prevented the entrance of air between the pipette stem and the stirrer, and ensured the presence of dry air within the apparatus throughout the determination. The composition of the solution was determined by volumetric analysis, as already described. Further samples were withdrawn at intervals of an hour until saturation was reached. As a rule, the first sample removed was found, on comparison with the later results, to be already saturated.

At each temperature the composition of the solid phase was determined in the manner given in the first section.

The results of the determinations are embodied in the following table:

Temperature.	Solid phase.	Grams of anhydrous lithium chloride dissolved by 100 grams of ethyl alcohol.
0°	$\text{LiCl} \cdot 4\text{C}_2\text{H}_5\text{O}$	14.42
5	$\text{LiCl} \cdot 4\text{C}_2\text{H}_5\text{O}$	15.04
10	$\text{LiCl} \cdot 4\text{C}_2\text{H}_5\text{O}$	16.77
15	$\text{LiCl} \cdot 4\text{C}_2\text{H}_5\text{O}$	18.79
17	$\text{LiCl} \cdot 4\text{C}_2\text{H}_5\text{O}$	20.31
20	LiCl	24.28
30	LiCl	25.10
40	LiCl	25.38
50	LiCl	24.40
60	LiCl	23.46

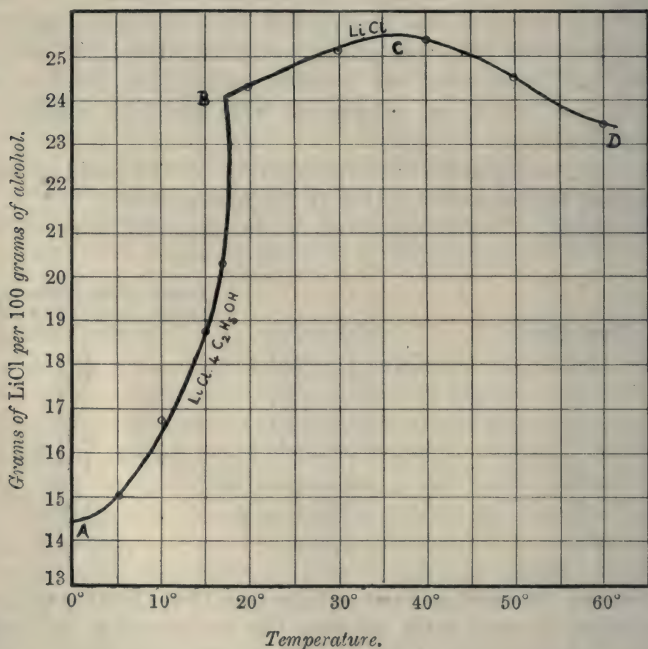
From the numbers given it will be seen that the rate of increase of solubility is most rapid between the temperatures 15° and 20° , and the determination at 17° was afterwards made both to confirm this rapid rise and to fix the position of the first portion of the solubility curve, which is produced below.

The full curve *ABCD* consists of two separate portions intersecting at *B*, the point which indicates the transition point of the alcoholate. Read from the curve, the change point is 17.4° , and this temperature received confirmation by experiments on the growth or disappearance of the crystalline phase, $\text{LiCl} \cdot 4\text{C}_2\text{H}_5\text{O}$. For this purpose the behaviour of a mixture of the solution, and the crystalline and anhydrous solid phases contained in a tightly-closed vessel was closely watched as the temperature was very slowly

altered over the range 17—18°. The deposition of the crystalline form was found clearly to occur up to a temperature of 17·1°, whilst at 17·6° the anhydrous slowly grew at the expense of the crystalline variety. Confirmation was made of these visual tests by analysis, and it was proved that at 17·6° the anhydrous salt formed the solid phase, whilst at 17·1° it consisted of the alcoholate. The transition point accordingly lies at about 17·4°.

The Comparative Solubilities at 25°.

The method adopted in measuring the solubilities at 25° was very similar to that in a former investigation (Peddle and Turner,



this vol., p. 1202), excess of the very finely powdered and thoroughly dried salts being agitated in small, perfectly ground, stoppered bottles with the alcohol used as solvent. Initially the mixture was maintained for some time at 40°, then transferred to the thermostat at 25°, and thoroughly agitated from time to time. Samples for analysis were first withdrawn after forty-eight hours and then afterwards at twenty-four-hour intervals, the total period of the test extending usually to nine or ten days. The amounts of solution removed for analysis varied from 0·5 to 5 grams for

the more soluble substances, and as much as 20 or 60 grams with the salts only sparingly soluble in propyl or *iso*amyl alcohols. Before the aqueous solution of the sample was prepared for analysis, the alcohol was removed by evaporation, save, as happened with the iodide solutions, when decomposition of the salt began as a result of the evaporation. Despite the use of brown-coloured bottles, the iodide solutions after some days developed a brown tint due to traces of iodine.

In one instance, namely, the solubility of lithium iodide in amyl alcohol, the method employed was that used in determining the solubility curve of lithium chloride in ethyl alcohol, for the viscosity of the solution prevented rapid diffusion through the liquid, and necessitated continuous stirring.

The collected results are given in the following table, the figures representing the number of grams of the anhydrous salt dissolved by 100 grams of the solvent. In order to compare the solvent action of the alcohols with that of water, determinations in the last-named solvent are included in the table. In four cases the solid phases actually present are not the anhydrous forms, but, in water, $\text{LiCl} \cdot \text{H}_2\text{O}$, $\text{LiI} \cdot 3\text{H}_2\text{O}$, and $\text{NaI} \cdot 3\text{H}_2\text{O}$; in propyl alcohol, $\text{LiI} \cdot 4\text{C}_3\text{H}_8\text{O}$.

Substance.	Solvent.				
	H_2O .	CH_3O .	$\text{C}_2\text{H}_5\text{O}$.	$\text{C}_3\text{H}_7\text{O}$.	$\text{C}_5\text{H}_{11}\text{O}$.
LiCl	83.37 ¹	42.36	25.83	16.22	9.03
LiI	168.5 ²	343.4	250.8	47.52	112.5
NaCl	36.05 ³	1.31	0.065	0.012	0.002
NaI	184.5 ⁴	90.35	46.02	28.22	16.30
KCl	39.90 ⁵	0.53	0.022	0.004	0.0008
KBr	67.75 ⁶	2.17	0.142	0.035	0.003
KI	148.3 ⁷	18.04	2.16	0.43	0.098
RbCl	94.35 ⁸	1.41	0.078	0.015	0.0025

¹ Kremers, *Ann. Phys. Chem.*, 1856, [ii], 99, 47.

² *Ibid.*, 1858, [ii], 103, 65.

³, ⁵ and ⁸ Berkeley, *Phil. Trans.*, 1904, 203, A, 206.

⁴ and ⁶ De Coppet, *Ann. Chim. Phys.*, 1883, [v], 30, 425.

⁷ Landolt-Börnstein "Tabellen," 1904.

Patten and Mott (*J. Physical Chem.*, 1904, 8, 157) made determinations, without describing the method, of the solubility of lithium chloride in a series of alcohols, but their results in two out of the three comparable cases are totally different from ours. Their figures for the percentage of the salt in the solution are, in ethyl alcohol, 2.475; in propyl alcohol, 3.720; in butyl alcohol, 9.56; in *iso*amyl alcohol, 8.26. There is close agreement between their value for *iso*amyl alcohol and ours, which when calculated to the percentage basis is 8.29, but unaccountable divergence in the other instances. All our measurements go to prove that the haloid salts

are decreasingly soluble as one passes from water along the series of alcohols. There is no regularity in Patten and Mott's figures.

A few other measurements are available for comparison; de Bruyn (*Zeitsch. physikal. Chem.*, 1892, **10**, 782) deduced from experiment the following solubilities, in grams dissolved by 100 grams of the solvent: sodium chloride, 1.41 in methyl and 0.065 in ethyl alcohol at 18.5°; sodium iodide, 77.7 and 43.1 respectively at 22.5°; potassium chloride, 0.5 and 0.034 at 18.5°; potassium bromide, 1.51 and 0.13 at 25°; potassium iodide, 16.5 and 1.75 at 20.5°. The values for sodium iodide and potassium bromide in methyl alcohol are both low, but in the other cases, allowing for temperature differences, there is fair agreement between our and de Bruyn's numbers.

For potassium iodide, Walden (*Zeitsch. physikal. Chem.*, 1906, **55**, 683) found values at 25°, in methyl alcohol 14.97, in ethyl 1.92, and our numbers, when reduced to the same basis, are in good agreement.

Turning now to a consideration of our data, three very clear regularities manifest themselves. First, with the single exception of lithium iodide, the solubility decreases as we pass from water and ascend the series of alcohols; and it must be remembered that the two numbers for lithium iodide which break the regularity of the series, namely, those in water and in propyl alcohol, are the solubilities for the hydrate and alcoholate respectively, whereas for the same substance and the other three alcohols the numbers represent the solubilities of the uncombined salt.

Next, solubility in water and the alcohols increases in the order chloride, bromide, iodide. There is no exception to this rule.

Finally, rubidium chloride shows an interesting divergence from the regular order in the series of the alkali chlorides, the order of solubilities being lithium chloride > sodium chloride > rubidium chloride > potassium chloride. This is true of all five solvents.

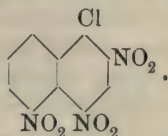
We desire to express our thanks to the Government Grant Committee of the Royal Society for a grant which assisted us to purchase solvents used in this investigation.

CHEMISTRY DEPARTMENT,
THE UNIVERSITY, SHEFFIELD.

CCV.—*Nitration of 1-Chloro-2:4-dinitronaphthalene.*

By MAX RINDL.

THE readiness with which 1-chloro-2:4-dinitronaphthalene can be prepared from Martius yellow by the action of *p*-toluenesulphonyl chloride and diethylaniline (Ullmann and Bruck, *Ber.*, 1908, **41**, 3932) has suggested the use of this material as the starting point in the preparation of trinitronaphthalene derivatives. By the nitration of chlorodinitronaphthalene a mixture of two isomeric chlorotrinitronaphthalenes is obtained. The relative quantities of these two products are such that one may be regarded as a by-product. The principal isomeride has the constitution:



Its chlorine atom is replaceable by the hydroxyl group, and the trinitronaphthol so formed yields on oxidation with nitric acid 3-nitrophthalic acid. The third nitro-group must therefore have assumed one of the α -positions in the unsubstituted benzene nucleus. The trinitronaphthol derived from the above chlorotrinitronaphthalene proves to be identical with the trinitronaphthol resulting from the treatment of 5-nitro-4-nitroso- α -naphthol with dilute nitric acid, and which has been proved to be 2:4:5-trinitro- α -naphthol (Graebe, *Ber.*, 1899, **32**, 2878).

The second product formed in the nitration process must be 1-chloro-2:4:8-trinitronaphthalene, since the trinitronaphthol derived from it is identical with the trinitronaphthol obtained by treating 8-nitro-4-nitroso- α -naphthol with dilute nitric acid (Graebe, *Ber.*, 1899, **32**, 2879).

Under the acidifying influence of the three nitro-groups the chlorine atom is extremely mobile. In this respect 1-chloro-2:4:5-trinitronaphthalene presents an analogy to picryl chloride; thus on boiling with a dilute aqueous solution of alkali hydroxide it is converted into trinitronaphthol. The replacement of the chlorine atom by the hydroxyl group can even be effected by sodium carbonate. The trinitronaphthol so obtained is a dye, but the expectation that the newly-introduced nitro-group would function as an auxochrome was not realised. The shade of colour is the same as that produced by Martius yellow, the intensity, however, being markedly diminished.

Other groups can be substituted for chlorine in 1-chloro-2:4:5-

trinitronaphthalene with the greatest facility, such as the methoxyl, amino-, and anilino-groups.

Experiments undertaken with a view to prepare dinaphthyl derivatives by removing the chlorine atom with finely-divided copper, and thus joining two naphthalene molecules, although not entirely successful, nevertheless demonstrated the possibility of thus obtaining dinaphthyl compounds. From 1-chloro-2:4:5-trinitronaphthalene, hexanitrodinaphthyl should have been formed. The investigation of the main product of the reaction was abandoned after repeated futile attempts at purification. An interesting secondary reaction, however, took place, resulting in the substitution of chlorine by hydrogen with the formation of 1:3:8-trinitronaphthalene, thus supplying additional evidence in favour of the constitution given above. In the case of 1-chloro-2:4-dinitronaphthalene, tetranitrodinaphthyl was easily obtained.

An interesting observation, which seems to indicate a case of steric hindrance, was made when attempting to reconvert the two trinitronaphthols into the chlorotrinitronaphthalenes from which they were originally prepared. Whilst *p*-toluenesulphonyl chloride and diethylaniline readily act on 2:4:5-trinitro- α -naphthol, not a trace of 1-chloro-2:4:8-trinitronaphthalene could be obtained from 2:4:8-trinitro- α -naphthol by similar treatment.

EXPERIMENTAL.

Nitration of 1-Chloro-2:4-dinitronaphthalene.

The chlorodinitronaphthalene prepared from 2:4-dinitro- α -naphthol was added in small portions to concentrated nitric acid (D 1.52), the acid being cooled by immersion in cold water. As the result of a large number of experiments, it was found that the maximum yield was obtained if the quantity of chlorodinitronaphthalene compared to that of nitric acid was as 1 to 2.5 or 3. After several days, transparent, hexagonal prisms of chlorotrinitronaphthalene began to separate out, which were collected from time to time and dried on porous plates. The first fraction, which was quite uniform, was subsequently shown to be 1-chloro-2:4:5-trinitronaphthalene. After a period, which varied slightly with the conditions of experiment—being on an average twenty-one days—amorphous, granular aggregates began to separate out, together with the prisms in gradually increasing quantities, the quantity of the prismatic substance meanwhile decreasing. The crops of prisms were recrystallised from glacial acetic acid, forming tiny, white needles with a tinge of yellow, and melting at 143–144°.

The substance is insoluble in light petroleum, sparingly soluble in alcohol, and readily so in benzene or acetic acid.

Found: C=40.40; H=1.70; N=14.22.

$C_{10}H_4O_6N_3Cl$ requires C=40.32; H=1.36; N=14.15 per cent.

Separation of the Isomeric Chlorotrinitronaphthalene.

A partial separation of the two isomeric chlorotrinitronaphthalenes which crystallise out together as the nitration process continues can be effected by fractional crystallisation from glacial acetic acid. The more sparingly soluble compound, melting at 143—144°, separates out first. By recrystallising the later fractions several times from the same solvent the second isomeride was obtained, although apparently not in a pure state. It melts between 118° and 126°.

Found: N=14.22; Cl=11.61.

$C_{10}H_4O_6N_3Cl$ requires N=14.15; Cl=11.91 per cent.

Conversion of 1-Chloro-2:4:5-trinitronaphthalene into 2:4:5-Trinitro- α -naphthol.

Three grams of finely divided 1-chloro-2:4:5-trinitronaphthalene (1 molecule) were suspended in a little water or alcohol, and boiled for half-an-hour after the addition of the theoretical quantity (20 c.c., corresponding with 2 molecules) of *N*/10-sodium hydroxide solution. Sodium hydroxide is preferable to potassium hydroxide on account of the greater solubility of the sodium salt of trinitronaphthol. As the conversion took place, the naphthol salt dissolved to a reddish-brown solution. After completion of the reaction the solution was concentrated, and decomposed with dilute hydrochloric acid. The yellow, flocculent precipitate was collected, washed with as little water as possible, and dried. When crystallised from acetic acid it formed yellow leaflets melting at 186° (corr. 190°). (Found, C=42.87; H=2.12; N=15.24. $C_{10}H_5O_7N_3$ requires C=42.98; H=1.81; N=15.09 per cent.)

On evaporating to dryness a suspension of the above compound in very dilute nitric acid, a residue of 3-nitrophthalic acid remained. This trinitronaphthol agrees in all its properties with the 2:4:5-trinitro- α -naphthol obtained by acting on 5-nitro-4-nitroso- α -naphthol with warm dilute nitric acid (Graebe, *Ber.*, 1899, 32, 2877), a mixture of the two showing no depression of the melting point.

Formation of 1:3:8-Trinitronaphthalene.

A solution of 1-chloro-2:4:5-trinitronaphthalene was treated with copper powder, with the object of obtaining hexanitrodinaphthyl, as follows:

Ten grams of the substance were dissolved in 40 grams of nitrobenzene and the solution was heated, after the addition of 10 grams of copper powder, for fifteen minutes under reflux. The hot solution was filtered, and the filtrate distilled in a current of steam in order to remove the nitrobenzene. The greyish-black solid residue was extracted for two days in a Soxhlet apparatus with benzene. The resinous, brown extract was concentrated and crystallised several times from glacial acetic acid with addition of animal charcoal. Finally, a solid was obtained melting at 212—213° (corr. 218—219°), which proved to be identical with 1:3:8-trinitronaphthalene (Beilstein and Kuhlberg, *Annalen*, 1873, **169**, 96; Friedländer, *Ber.*, 1899, **32**, 3531). (Found, N=16.17. $C_{10}H_5O_6N_3$ requires N=16.01 per cent.)

The dark residue remaining in the Soxhlet apparatus after extraction of the 1:3:8-trinitronaphthalene with benzene is insoluble in most solvents. It dissolves in hot concentrated nitric acid, but is reprecipitated in the same impure state. A solution in pyridine remained black and opaque even after boiling for hours with animal charcoal, and showed no tendency to crystallise on concentration. Addition of alcohol, acetic acid, and acetone produced only resinous, black precipitates. As a last resort, the solution was left for weeks over zinc chloride in a vacuum desiccator, but as no better results were realised the examination of this substance was discontinued.

Conversion of 2:4:5-Trinitro- α -naphthol into 1-Chloro-2:4:5-trinitronaphthalene.

The displacement of the hydroxyl group by chlorine can be effected by means of *p*-toluenesulphonyl chloride and diethylaniline in much the same way as has been done in the case of 2:4-dinitro- α -naphthol. A slight modification of the method adopted with the latter substance, however, is necessary.

2.8 Grams of 2:4:5-trinitro- α -naphthol (1 molecule) were thoroughly mixed with 2.85 grams of *p*-toluenesulphonyl chloride ($1\frac{1}{2}$ molecules), 6.4 c.c. of diethylaniline (4 molecules) were added, and the mixture was heated for an hour on the steam-bath with frequent stirring. After cooling, the unchanged diethylaniline was removed as the hydrochloride, by adding dilute hydrochloric acid, stirring, and decanting. A pasty mass remained, from which

unchanged *p*-toluenesulphonyl chloride was removed by boiling with a little alcohol. 1-Chloro-2:4:5-trinitronaphthalene remained as a brown powder, which was purified by washing with water, drying, treating with very dilute aqueous ammonia, and finally crystallising from glacial acetic acid. The product melted at 143—144°. (Found, N=13·95. Calc., N=14·15 per cent.)

2:4:5-Trinitro- α -naphthylamine.

In order to effect the replacement of chlorine by the amino-group, 1·5 grams of 1-chloro-2:4:5-trinitronaphthalene were dissolved in 50 c.c. of amyl alcohol, and gaseous ammonia was passed through the boiling solution. After a short time a yellow precipitate, consisting of a mixture of ammonium chloride and trinitronaphthylamine, began to fall. In order to complete the reaction it was necessary to continue passing the gas through for at least two hours. The alcohol was removed by distillation in a current of steam, and the precipitate collected and washed, until the filtrate ceased to show the chlorine reaction. When crystallised from acetone or glacial acetic acid with addition of animal charcoal the product formed microscopic, yellow prisms, melting at 305°, having previously changed colour to brown and black. An aqueous solution of alkali hydroxide converts the trinitronaphthylamine into the alkali salt of trinitronaphthol, which dissolves with a red colour. *2:4:5-Trinitro- α -naphthylamine* is insoluble in alcohol, toluene, or light petroleum, sparingly soluble in amyl alcohol or glacial acetic acid, and more readily so in acetone.

Found: C=43·23; H=2·47; N=19·94.

$C_{10}H_6O_6N_4$ requires C=43·13; H=2·18; N=20·19 per cent.

2:4:5-Trinitro- α -phenylnaphthylamine.

Aromatic amines condense with 1-chloro-2:4:5-trinitronaphthalene to form trinitroarylnaphthylamines. One molecular proportion of chlorotrinitronaphthalene was dissolved in a little benzene, and two molecular proportions of aniline were added. The colour changed to red, a violent reaction set in, and the whole mass solidified. In order to remove the aniline hydrochloride formed in the reaction the product was boiled with water. The red, crystalline residue was collected, dried, and recrystallised from glacial acetic acid, from which it separated in plates melting at 218·5°. It is insoluble in ether, alcohol, or light petroleum, but moderately soluble in benzene or glacial acetic acid.

Found: C=54·39; H=3·12; N=15·96.

$C_{16}H_{10}O_6N_4$ requires C=54·20; H=2·85; N=15·85 per cent.

2:4:5-Trinitro- α -naphthylethylamine.

One gram of 1-chloro-2:4:5-trinitronaphthalene (1 molecule) was dissolved in a little alcohol, and 1.35 grams (3 molecules) of a 33 per cent. alcoholic solution of ethylamine were added. The colour changed to red, and a precipitation of yellow, interlaced needles began. The mixture was kept boiling for about fifteen minutes, filtered, and the precipitate crystallised from benzene or alcohol. The substance melts at 157—159°. It is only very sparingly soluble in ether, but readily so in glacial acetic acid, and is hydrolysed on heating with concentrated solutions of alkali hydroxides.

Found: C=47.18; H=3.42; N=18.46.

$C_{12}H_{10}O_6N_4$ requires C=47.02; H=3.30; N=18.34 per cent.

2:4:5-Trinitro- α -naphthyl dimethylamine.

The condensation with dimethylamine was effected in the same way as described above for ethylamine. The product crystallised from glacial acetic acid in minute, orange leaflets, melting at 194.5—195.5°.

Found: N=18.40.

$C_{12}H_{10}O_6N_4$ requires N=18.34 per cent.

2:4:5-Trinitro- α -naphthyl Methyl Ether.

Two grams of 1-chloro-2:4:5-trinitronaphthalene were dissolved in 75 c.c. of methyl alcohol, and to the boiling solution the theoretical quantity (0.36 gram) of sodium methoxide, dissolved in 25 c.c. of methyl alcohol, was added drop by drop. The red solution was boiled for fifteen minutes and cooled, when yellow crystals separated. On recrystallisation from acetic acid these melted at 150.5—151.5°.

Found: C=44.85; H=2.71; N=14.16.

$C_{11}H_7O_7N_3$ requires C=45.02; H=2.41; N=14.37 per cent.

1:3:5-Trinitronaphthol from 1-Chloro-2:4:8-trinitronaphthalene.

In order to determine the constitution of the isomeric chlorotritronaphthalene, formed as a by-product in the process of nitration, this substance was converted into trinitronaphthol by treatment with an aqueous solution of sodium hydroxide. The method adopted was exactly the same as in the case of 1-chloro-2:4:5-trinitronaphthalene. The product of the reaction was impure, and had to be recrystallised several times from glacial acetic acid before a homogeneous trinitronaphthol was obtained, indicating that the chlorotritronaphthalene was not uniform, in spite of the repeated frac-

tional crystallisation. The trinitronaphthol ultimately obtained proved to be identical with that derived from 8-nitro-4-nitroso- α -naphthol. The by-product of the nitration is therefore 1-chloro-2:4:8-trinitronaphthalene.

It seemed interesting to obtain a criterion of the degree of purity of the 1-chloro-2:4:8-trinitronaphthalene by comparing it with the pure product obtained from pure 2:4:8-trinitro- α -naphthol by treatment with *p*-toluenesulphonyl chloride and diethyl-aniline. The method applied was identical with that adopted in the case of 2:4:5-trinitro- α -naphthol, except that a series of experiments was carried out with varying quantities of the reacting substances. In all cases the unaltered trinitronaphthol was recovered, not a trace having undergone conversion. It is suggested that this might be a case of steric hindrance, due to the nitro-groups in the ortho- and peri-positions.

2:4:2':4'-Tetranitro- $\alpha\alpha$ -dinaphthyl.

In view of the failure to obtain hexanitrodinaphthyl, an attempt was made to couple two chlorodinitronaphthalene molecules together, by heating a solution with copper powder.

Five grams of 1-chloro-2:4-dinitronaphthalene were dissolved in 10 c.c. of nitrobenzene, heated, after the addition of 5 grams of copper powder, for thirty minutes under reflux. After filtration, the filtrate was distilled in a current of steam, and the dark grey residue extracted with ether for several days. From the ethereal extract 2.4 grams of 1:3-dinitronaphthalene were obtained. The residue remaining in the Soxhlet apparatus was dissolved in a considerable quantity of benzene, and, after concentration, was allowed slowly to evaporate. Dark greyish-brown scales separated, which were collected from time to time, dissolved in pyridine, and boiled for an hour with animal charcoal. After concentrating the filtered solution, alcohol was added, when yellow, interlaced needles were precipitated. 2:4:2':4'-Tetranitro- $\alpha\alpha$ -dinaphthyl remained unchanged when heated to 350°. It is sparingly soluble in benzene or acetic acid, more readily so in nitrobenzene or pyridine.

Found: C=55.52; H=2.52; N=13.16.

C₂₀H₁₀O₈N₄ requires C=55.27; H=2.33; N=12.93 per cent.

The author desires to thank Professor Ullmann, of the Königl. Technische Hochschule, Charlottenburg, for kind encouragement and advice during the course of this work.

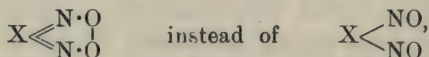
GREY UNIVERSITY COLLEGE.

BLOEMFONTEIN, SOUTH AFRICA.

CCVI.—*Constitution of Furoxans (Dioxime "Peroxides")*.

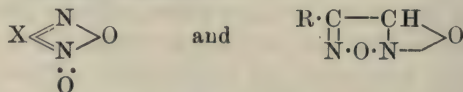
By MARTIN ONSLOW FORSTER and MATTHEW FELIX BARKER.

IN a communication dealing with the nature of the compounds which arise by heating the *o*-nitrotriazole-derivatives of benzene and naphthalene (Forster and Fierz, T., 1907, **91**, 1942), it was suggested that the numerous aromatic substances previously regarded as dinitroso-compounds should be classified as dioxime peroxides:



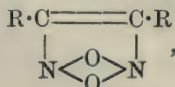
and this proposal remained unchallenged until Green and Rowe (T., 1912, **101**, 2452) claimed for these materials the constitution of furoxans (oxides of furazan), similar in constitution to the aliphatic derivatives described by Wieland and Semper (*Annalen*, 1907, **358**, 36).

During the discussion which followed their paper, however, it was pointed out by one of us that the particular oxide of furazan adopted by Green and Rowe, like the one previously advocated by Wieland and Semper, namely:



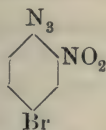
respectively, conflicts with the observation of Forster and Fierz (*loc. cit.*) that when 1-nitro-2-naphthylazoimide and 2-nitro-1-naphthylazoimide are heated, elimination of nitrogen leads to the same dioxime "peroxide" in each case, an origin which points unmistakably to a symmetrical constitution for the furazan oxide.

A reasonable objection to this argument, however, follows from the fact that the transference of oxygen from one atom of nitrogen to the other, demanded in the case of the nitronaphthylazoimides if the formula of Green and Rowe is correct, might be due to the steric effect of the second benzene ring, and we have therefore made experiments to ascertain whether the change in question is independent of the naphthalene nucleus. We find that it is, and are therefore led to the conclusion that these furazan oxides are symmetrical in structure. As stated in a preliminary communication (P., 1913, **29**, 152), we believe the formula:



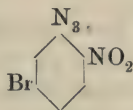
to be the most satisfactory representation of these compounds, a conviction in which we are now supported by Green and Rowe (this vol., p. 897), whose preliminary announcement appeared simultaneously with our own.

The authors mentioned base their conclusion on the course followed by the oxidation of *o*-nitroamines with alkaline sodium hypochlorite. They produced the same tolufurazan oxide alike from *p*-nitro-*m*-toluidine and *m*-nitro-*p*-toluidine, whilst from *m*-chloro- and *p*-chloro-*o*-nitroanilines the same chlorobenzfurazan oxide was obtained. Our inquiry depends on the decomposition of *o*-nitroazoimides. Having first repeated the earlier experiments with 1-nitro-2-naphthylazoimide and 2-nitro-1-naphthylazoimide, assuring ourselves that the same naphthafurazan oxide arises from both, two bromonitrophenylazoimides:



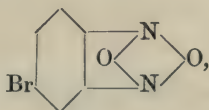
M. p. 80°.

and

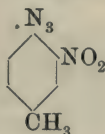


M. p. 66°.

were prepared, and found to yield the same bromobenzfurazan oxide,

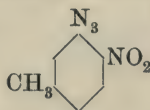


when heated. Furthermore, from the isomeric nitrotriazotoluenes,



M. p. 38°.

and

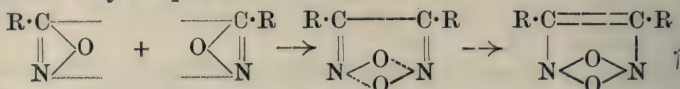


M. p. 87°.

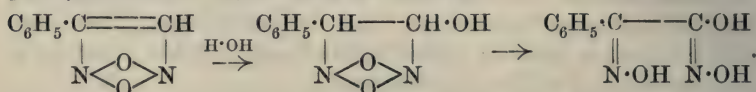
the tolufurazan oxide prepared by Green and Rowe from the nitro-toluidines has been obtained, and it seems to us that all these experiments taken together place the symmetrical structure of the aromatic furazan oxides on a firm basis.

Whether this conclusion is applicable also to the aliphatic compounds of Wieland and Semper cannot be stated so definitely, but there is much in favour of extending it to these derivatives; for instance, the statement that the most general and most important source of the dioxime "peroxides" is the polymerisation of the nitrile oxides (*Annalen*, 1907, **358**, 37) involves, on the basis of the formula put forward by those authors, behaviour different on the part of one molecule from that of another, which appears

improbable, whereas according to our formula the polymerisation would be very simple:

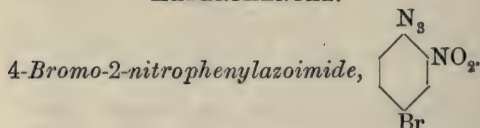


Furthermore, decomposition of diphenylglyoxime "peroxide" into phenylcarbimide (2 mols.) is more in accordance with a symmetrical structure, whilst the action of alkali on phenylfuroxan, leading to oximinobenzoylformhydroxamic acid (*loc. cit.*, p. 59), would be represented as follows:



Green and Rowe found that with hydroxylamine the furazan oxides may be reduced to the dioximes, a change which takes place also when reduction is effected with zinc dust and a limited amount of acetic acid (Forster, T., 1903, **83**, 525). We have studied the behaviour of these compounds towards hydrazine hydrate, which leads in some cases to the furazan, in others to the diamine.

EXPERIMENTAL.



4-Bromo-2-nitroaniline (6.5 grams) suspended in a mixture of glacial acetic acid (40 c.c.) and sulphuric acid (20 c.c.) was treated with ice and solid sodium nitrite until a clear solution was formed. Excess of nitrite having been destroyed with carbamide, aqueous sodium azide (4 grams) was added, when the substituted azoimide was precipitated in very pale yellow crystals. After recrystallisation from cold acetone diluted with water, followed by precipitation from cold benzene with petroleum, a felted mass of almost colourless needles was formed, melting at 80°:

0.1972 gave 38.3 c.c. N₂ at 13.5° and 766 mm. N = 23.2.

C₆H₃O₂N₄Br requires N = 23.1 per cent.

The substance is freely soluble in cold benzene or acetone, less readily in methyl or ethyl alcohol, and very sparingly soluble in petroleum.

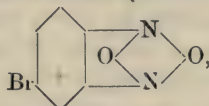
Decomposition by Heat.—In quantities of 2 decigrams, 4-bromo-2-nitrophenylazoimide was heated at 80–90°, the temperature being raised very gradually to 110° as the liberation of nitrogen

slackered. On extracting with warm petroleum (b. p. 60—80°), only a very slight tarry residue was left, the solvent depositing opaque masses of pale yellow, lustrous prisms, melting at 69°:

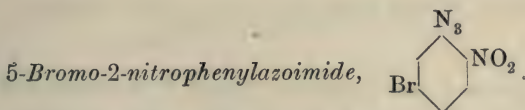
0.2004 gave 21.4 c.c. N_2 at 15° and 775 mm. $N=12.9$.

$C_6H_3O_2N_2Br$ requires $N=13.0$ per cent.

4-Bromobenziisooxadiazole oxide (4-bromobenzfurazan oxide),



is freely soluble in cold organic media excepting petroleum.



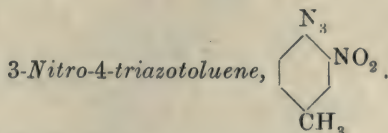
The base required for making this material was prepared by heating 2:4-dibromo-1-nitrobenzene with alcoholic ammonia during two days at 150°, unchanged dibromonitrobenzene being removed by extracting the product several times with warm petroleum, in which 3-bromo-6-nitroaniline is only sparingly soluble. Conversion into the substituted phenylazoimide was effected by the process used in the case of the isomeride, the pale yellow oil precipitated from the diazonium solution by sodium azide solidifying almost immediately. The substance melts at 66°:

0.2000 gave 39.5 c.c. N_2 at 15° and 751 mm. $N=22.9$.

$C_6H_3O_2N_4Br$ requires $N=23.1$ per cent.

5-Bromo-2-nitrophenylazoimide is freely soluble in cold benzene, acetone, or ethyl acetate, and dissolves readily in warm petroleum (60—80°), separating in pale yellow, transparent plates or rectangular prisms.

Decomposition by Heat.—Proceeding as before, the substituted phenylazoimide was transformed into 4-bromobenziisooxadiazole oxide melting at 69°, not depressed by admixture with the product of heating 4-bromo-2-nitrophenylazoimide.



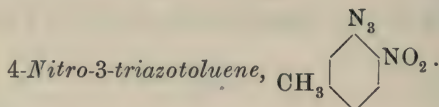
Diazotised nitrotoluidine ($CH_3:NO_2:NH_2=1:3:4$) was treated in the manner described above, when the azoimide separated as an oil, which rapidly solidified; after recrystallisation from acetone

and finally from alcohol, diluted in each case with water, it separated in long, pale yellow needles, melting at 38°:

0.1307 gave 36.0 c.c. N_2 at 24° and 764 mm. $N=31.5$.

$C_7H_6O_2N_4$ requires $N=31.5$ per cent.

Decomposition by Heat.—When heated carefully the azoimide began to effervesce at 70—75°, and decomposition became complete after raising the temperature to 110°; recrystallisation from hot petroleum (80—100°) gave a specimen of tolufurazan oxide melting at 96° (Green and Rowe give 97°).



The substituted azoimide was derived from diazotised nitrotoluidine ($CH_3:NO_2:NH_2=1:4:3$) in the usual manner, and after recrystallisation from cold acetone diluted with water separated in pale yellow needles melting at 87°:

0.1202 gave 33.9 c.c. N_2 at 26° and 763 mm. $N=31.5$.

$C_7H_6O_2N_4$ requires $N=31.5$ per cent.

Decomposition by Heat.—A somewhat higher temperature was required to complete this change; gas was liberated most freely at 90—100°, and 110—120° was finally attained. Some tar remained after extracting with hot petroleum (80—100°), which deposited the tolufurazan oxide melting at 96°, identical with the product from 3-nitro-4-triazotoluene.

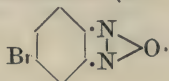
Behaviour of the Furazan Oxides towards Hydrazine Hydrate.

Benzfurazan oxide, prepared by heating *o*-nitrophenylazoimide, was treated in alcoholic solution with considerable excess of hydrazine hydrate, when the liquid became dark red; effervescence began, and became vigorous on gentle warming. After five to six hours on the water-bath the liquid remained clear on dilution, and was then evaporated to dryness; on extracting the residue with hot petroleum (60—80°) the latter deposited *o*-phenylenediamine in lustrous, rectangular plates melting at 103°. Similarly, tolufurazan oxide (m. p. 96°) gave tolylenediamine ($CH_3:NH_2:NH_2=1:3:4$) melting at 89°, and *p*-benzoquinonedioxime "peroxide" gave *p*-phenylenediamine melting at 141°.

In the case of naphthafurazan oxide, however, arising alike from 2-nitro-1-naphthylazoimide and 1-nitro-2-naphthylazoimide, 1:2-naphthylenediamine was not produced, the product consisting of naphthafurazan (m. p. 79°), the anhydride of naphthaquinone-

dioxime (Found, $N=16.5$; $C_{10}H_6ON_2$ requires $N=16.5$ per cent.). This compound has a marked odour of bitter almonds, a property which has hitherto escaped notice.

4-Bromobenzisooxadiazole (4-Bromobenzfurazan),



On adding hydrazine hydrate (5 c.c.) to a solution of bromobenzfurazan oxide (2 grams) in alcohol (40 c.c.) a deep red colour was developed, and gas was liberated; after being gently warmed during three to four hours, water precipitated long, yellow needles, melting at 75° after recrystallisation:

0.1473 gave 17.5 c.c. N_2 at 15° and 773 mm. $N=14.2$.

$C_6H_3ON_2Br$ requires $N=14.1$ per cent.

The substance has a distinct odour of menthol; it is freely soluble in most organic media, and does not reduce ammoniacal silver oxide.

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CCVII.—Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part IV.* The Rotations of the Normal Secondary Alcohols of the Formula $C_2H_5 \cdot CH(OH) \cdot R$.

By ROBERT HOWSON PICKARD and JOSEPH KENYON.

SEVERAL optically active carbinols of the general formula $R^1 \cdot CH(OH) \cdot R^2$ have already been synthesised and described (*loc. cit.*); of these, ten belong to the series of the formula



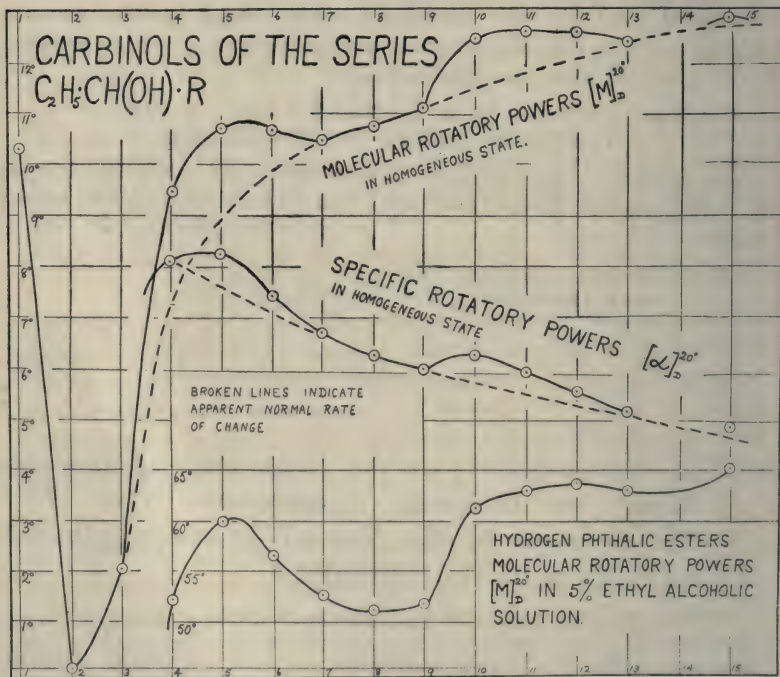
(hereafter called the "methyl" series), and eight belong to the series of the formula $CH(CH_3)_2 \cdot CH(OH) \cdot R$ (hereafter called the "isopropyl" series) (where R in each case represents a normal aliphatic radicle). Another series containing thirteen similar carbinols of the formula $C_2H_5 \cdot CH(OH) \cdot R$ having been now prepared, it is possible to contrast the rotatory powers of the members

*. For Part I of this series see T., 1911, **99**, 45; Part II, T., 1912, **101**, 620, and Part III, *ibid.*, 1427.

of this "ethyl" series with those of the members of the "methyl" and "isopropyl" series, since the corresponding members of each series only differ from one another as regards chemical constitution in containing the methyl, isopropyl, or ethyl groups.

In Fig. 4 (p. 1929) it will be seen that in the "methyl" series $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{R}$, where $\text{R}=\text{propyl}$ to undecyl, the molecular rotatory powers of the carbinols in the homogeneous state (at least at the boiling points) increase regularly as the molecular weight

FIG. 1.



Number of carbon atoms in growing chain R.

and size of the growing chain R increases, whilst the figures in table I, Part II, and Fig. 3 (p. 1927) show that in the "isopropyl" series the molecular rotatory powers of the carbinols in the homogeneous state increase rapidly until $\text{R}=\text{butyl}$, the higher members of the series having molecular rotatory powers only slightly higher than, or possibly equal to, that of the member with $\text{R}=\text{butyl}$.

It is now found that in the homogeneous state the molecular rotatory powers of the members of the ethyl series (see table I and Fig. 1) offer a decided contrast to those of each of the other series.

They increase slowly but definitely as the growing chain R increases in size from propyl to (at least) pentadecyl, but in addition to this normal increase (indicated by the dotted line in Fig. 1), there is a further increase in the molecular rotatory power exhibited by those members of the series in which the growing chain contains 5 (or 6), 10 (or 11), and 15 carbon atoms. This exaltation from the normal increase is greater when the growing chain contains five than when it contains ten carbon atoms, and is far less pronounced in the member containing fifteen carbon atoms in the growing chain.

TABLE I.

Rotatory Powers of the Normal Secondary Alcohols of the Formula
 $C_2H_5 \cdot CH(OH) \cdot R$.

R. (A normal alkyl group.)	In the homogeneous state.				Dispersion. $\alpha_D/\alpha_{H_2O \text{ green.}}$	In 5 per cent. solution in	
	$[\alpha]_D^{20^\circ}$	$[M]_D^{20^\circ}$	$[\alpha]_{gr}^{20^\circ}$	$[M]_{gr}^{20^\circ}$		ethyl alcohol $[M]_D^{20^\circ}$	benz- ene. $[M]_D^{20^\circ}$
Methyl	13.87°	10.30	16.09	11.91	0.845	10.77	10.44
Ethyl.....			Optically inactive.				
Propyl	1.97	2.01	2.24	2.29	(0.88)‡	1.17	1.87
Butyl.....	8.13	9.43	9.58	11.11	0.850	11.17	10.80
Amyl ..	8.22	10.69	9.64	12.53	0.856	14.47	13.26
Hexyl	7.38	10.63	8.63	12.43	0.858	13.86	13.82
Heptyl	6.68	10.58	7.76	12.26	0.864	9.81	12.11
Octyl.....	6.25†	10.74†	7.23	12.43	0.863	10.69	12.18
Nonyl	5.97†	11.09†	6.92	12.86	0.866	11.35	12.48
Decyl.....	6.23†	12.44†	7.21	14.42	0.865	13.46	14.62
Undecyl	5.87†	12.56†	6.80	14.55	0.865	13.38	15.30
Dodecyl	5.53†	12.61†	6.40	14.59	0.865	12.44	15.32
Tridecyl	5.11†	12.38†	5.92	14.32	0.863	12.75	15.44
Tetradecyl.....		(Has not been prepared)					
Pentadecyl	4.77†	12.88†	5.49	14.83	0.865	12.91	16.63

* These figures represent the average value of the rotatory dispersive powers calculated at intervals of 20° from 20° to 160° (or to the boiling points of the carbinols) as given in table II.

† Values at 20° extrapolated from curves based on observations recorded on p. 1954. These carbinols melt at about or above 20°.

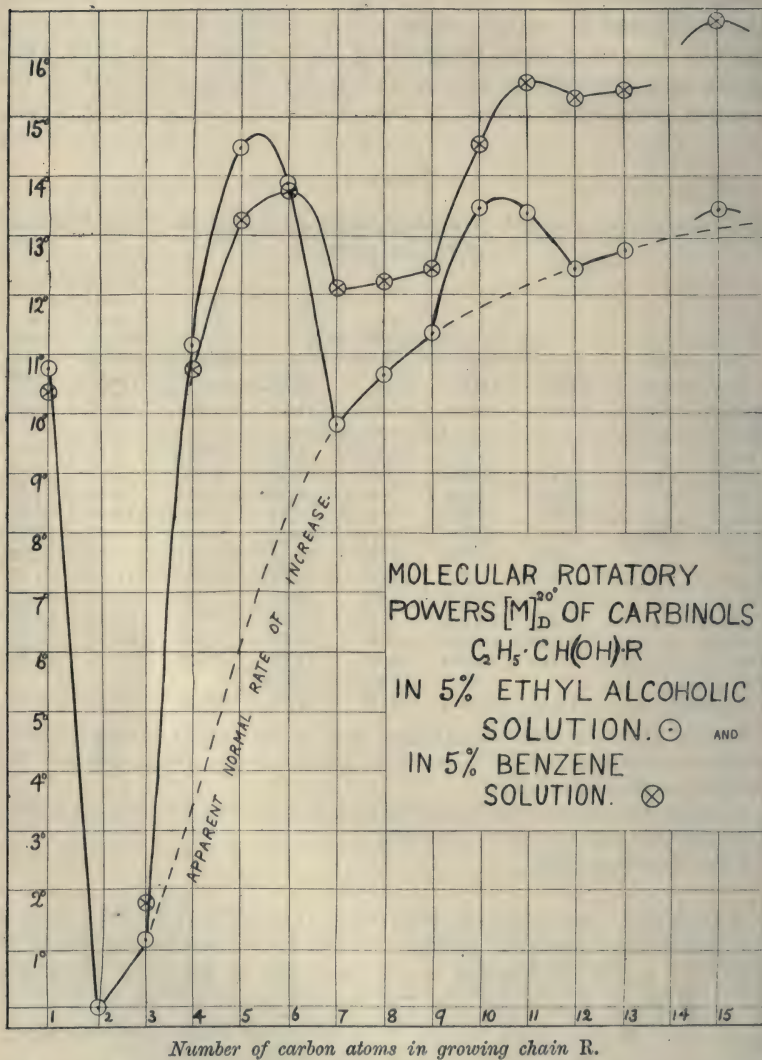
‡ See footnote, p. 1931.

Frankland has already suggested (T., 1899, 75, 368) that a maximum (or constant) rotatory power in a homologous series of optically active compounds would probably be attained when the growing chain contained five or six carbon atoms, since it is at that part of the series where it is expected from stereochemical considerations that the growing chain would all but return on itself. Our results appear to show conclusively that in the "ethyl" series, $C_2H_5 \cdot CH(OH) \cdot R$, there is a continuous gradual increase in the molecular rotatory powers as the growing chain increases, with

a further special exaltation each time that the growing chain of carbon atoms returns on itself.

When discussing some of our previous results, Frankland (T.,

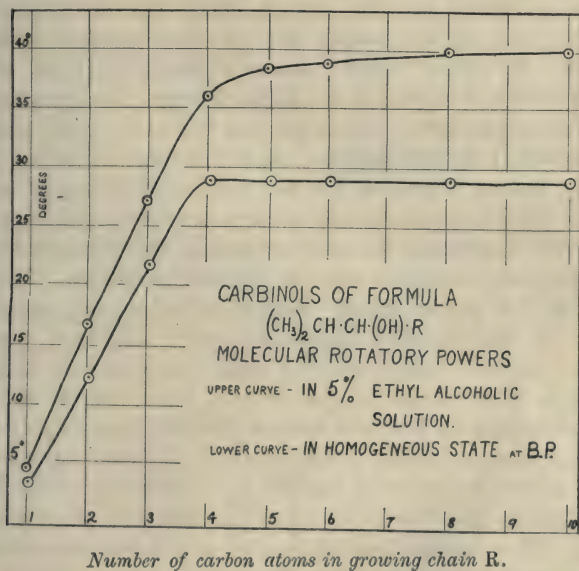
FIG. 2.



1912, 101, 660) suggested that some solvents like alcohol might "permit of a more unrestricted development of the rotatory effect of the homologous group (growing chain) than is the case when the

same compounds are examined in the liquid condition." This is actually the case when these carbinols are examined in ethyl-alcoholic solution. Thus, as will be seen from Fig. 2, the values of the rotatory powers of the members of the "ethyl" series follow those obtained when they were examined in the homogeneous state, but the effect due to the special stereochemical configuration of the growing chain when this contains about five or ten carbon atoms is much more pronounced. Similar results are obtained when the carbinols are examined polarimetrically in benzene solution. This same effect is also to be observed when the carbinols of the *isopropyl* series are examined in ethyl-alcoholic solution.

FIG. 3.

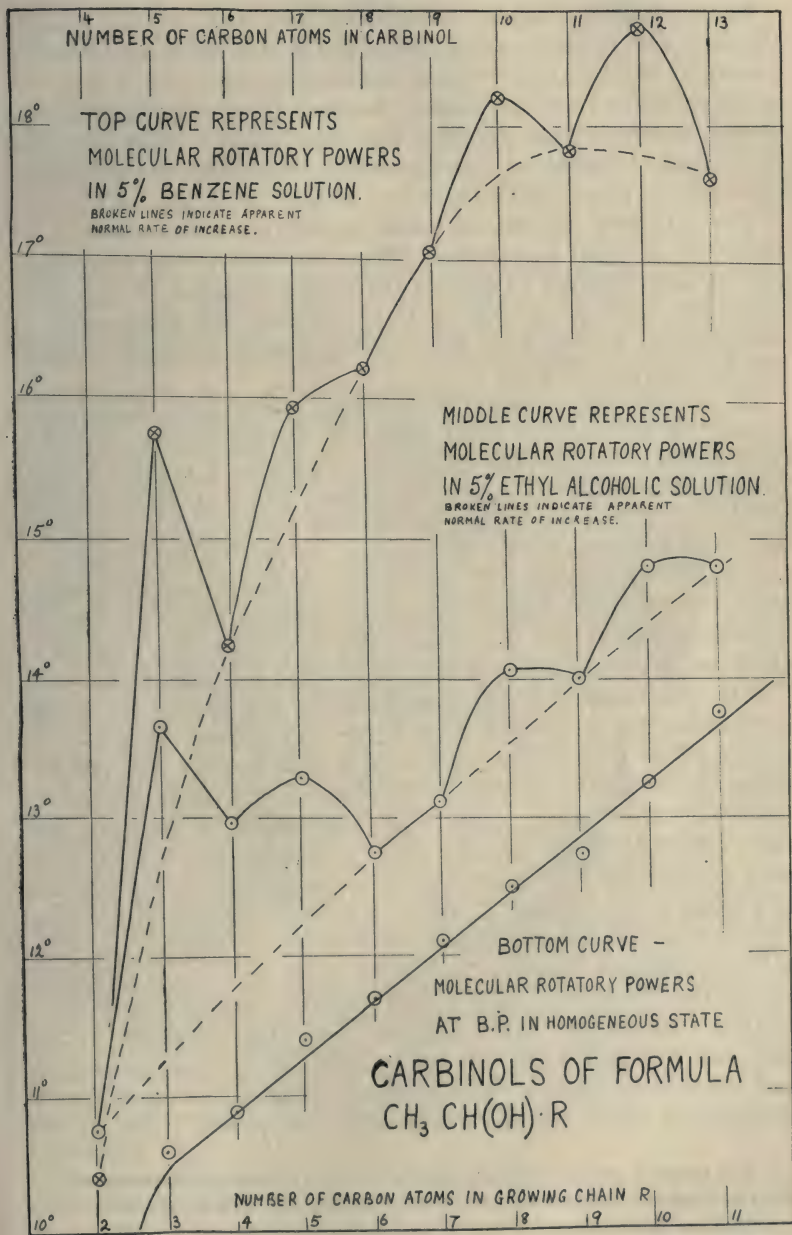


Thus (see Fig. 3), in the homogeneous state, an approximately constant value of the molecular rotatory power is reached for the butyl member, but in ethyl alcohol it is at the amyl member that the approximately constant value of the molecular rotatory power is attained. When the members of the "methyl" series are examined in ethyl alcohol or in benzene, the values obtained for the molecular rotatory powers (Fig. 4) are at first sight very confusing. Maxima on the irregular curves will be observed corresponding with methylpropylcarbinol, methylamylcarbinol, methyloctylcarbinol, and methyldecylcarbinol, and the curves are in striking contrast to the regular curve show-

ing the values of the molecular rotatory powers determined at the boiling point of the carbinols in the homogeneous state. The maxima on these curves, corresponding with methylamyl- and methyldecyl-carbinols are, of course, to be attributed to the special configuration of the growing chain. However, adopting a different nomenclature, methylpropylcarbinol, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{C}_3\text{H}_7$, and methyloctylcarbinol, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{C}_8\text{H}_{17}$, can be designated pentan- β -ol and decan- β -ol. It will now be seen that the maxima corresponding with these two carbinols containing five and ten carbon atoms respectively in the molecule can be attributed to the special configuration of the *normal chain of carbon atoms comprising the whole molecule*. So that the polarimetric examination of these solutions has afforded most conclusive evidence of the special effect that a normal chain of five (or ten) carbon atoms has on the rotatory power of a compound. In the "ethyl" series $\text{C}_2\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{R}$, a similar effect where the compounds (as distinct from the growing chain) contain five or ten carbon atoms, has not been observed—pentan- γ -ol (diethylcarbinol) is symmetrical, and therefore optically inactive, whilst the values obtained for the molecular rotatory power of decan- γ -ol (ethylheptylcarbinol) occupy a normal position on the three curves illustrating the observations in the homogeneous state, in ethyl-alcoholic solution and in benzene solution. The results recorded in this paper appear then to afford a very striking confirmation of Frankland's suggestion made fourteen years ago. Although this was based on the then conventional idea of the rigid tetrahedron model of the carbon atom, yet it, in common with theories such as Baeyer's Strain Theory, is not upset by more modern conceptions of the carbon atom. The carbon atom can be imagined to be a sphere with valency (or combining force) radiating from the centre like "lines of force" to the surface of the sphere (Werner). The further postulation of a greater concentration of the forces about the points of contact of the sphere with a regular tetrahedron circumscribed by it would explain perhaps better than the older idea of the rigid tetrahedron model the peculiar effect of a chain containing about five carbon atoms on the rotatory power of the compound.

The opinion of the authors, expressed in Part I (p. 47, *loc. cit.*), that in a reinvestigation of the problem of the relation between rotatory power and chemical constitution it was desirable to restrict the polarimetric examinations to those of liquids in the homogeneous state is now shown to be untenable. It is obvious that some effects due to the configuration of the molecule are only to be observed in solution, and are marked at all temperatures up

FIG. 4.



to the boiling point, when the compounds are examined in the homogeneous state.*

There does not appear to be any simple numerical relation between the various values obtained for the molecular rotatory powers of the members of these homologous series, and it does not seem probable from the results obtained (even after giving due weight to the obvious objection that they relate to only one class of compounds) that any such numerical relation exists between the rotatory powers of the members of any homologous series.

The following hypothesis based merely on a consideration of the space occupied by the four groups attached to the asymmetric carbon atom appears to explain the results obtained for the three series of carbinols as well as those obtained for eight series of simple esters derived from the "methyl" series of carbinols which will be described in Part V.

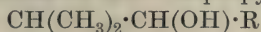
In a homologous series of optically active compounds represented by $Cabcd$, the usual effect of increasing the size of d (representing the growing chain) is to alter in a regular manner (usually to increase) the molecular rotatory power of the compounds. When the groups (or atoms) represented by a , b , and c occupy a relatively small space, as, for example, in the "methyl" series of carbinols, $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{R}$, the values of the molecular rotatory powers of the homogeneous compounds increase regularly with the increasing size of the chain, and only in solution are affected by the peculiar configuration of the chain, when this returns on itself.

When, however, the space occupied by the groups (or atoms) represented by a , b , and c is larger, the increase in molecular rotatory power as d increases in size may become less regular; either (i) it may be specially affected, when the chain returns on itself, as in the "ethyl" series, $\text{C}_2\text{H}_5 \cdot \text{CH}(\text{OH}) \cdot \text{R}$, or (ii) there may be a relatively large increase until d contains five carbon atoms with an increase of a much smaller order beyond, as, for example, in a series of esters, such as those of *sec.*-octyl alcohol with normal aliphatic acids,† in which there is a large increase in the value of the molecular rotatory power for each member of the series up to the *n*-valerate, and a still further, but relatively much smaller, increase for each member from the valerate to the palmitate; or (iii) when the space occupied by the groups a , b , and c is still greater, an "approximate maximum" is reached when the growing chain contains fewer than five carbon atoms, as, for

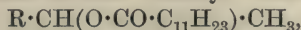
* This point has an obvious bearing on the assumed connexion between association and alteration of rotatory power in various solvents, and will be discussed in the next paper of this series.

† See Part V.

example, for the carbinols of the "isopropyl" series,



(when these are examined in the homogeneous state), and in a series* of *n*-dodecoates of the "methyl" carbinols,



in both of which the values of the molecular rotatory power increase rapidly up to that for the member with R containing four carbon atoms with a much smaller increment for the higher members.

Optical Dispersion.

The rotations of the carbinols of the three series have been determined for yellow (sodium) and green (mercury) light at temperatures from 20° to 160° (or to the boiling points of the carbinols). For each carbinol the dispersion value appears to be a constant (within the possible experimental error) over the range of temperature employed. Similar results have now been obtained by the authors in the case of ten series of compounds, so that optical dispersion may be considered generally to be independent of the temperature, as Walden has already assumed from his investigation of five esters of ricinoleic acid (*Ber.*, 1903, **36**, 781). The differences in the values of the dispersive power of the various members of a series of homologous compounds do not run parallel with the variations in the rotatory powers; thus, in the "methyl" series, all the members from the propyl to the undecyl have the same dispersive power (yellow/green 0·847), whilst that for the ethyl member is slightly less (0·840). Similar results have been obtained for the "isopropyl" series, each of the carbinols from the ethyl to the decyl member of this series having the same value for the dispersion (0·842), which varies from that of the methyl member; whereas in the "ethyl" series the methyl member (which is, of course, the ethyl member of the "methyl" series) with the value 0·840, and the propyl member with the value 0·88,† have dispersive powers varying widely from those of the butyl, amyl, and hexyl members, which have yellow/green values 0·850, 0·856, 0·858 respectively, thus approaching the constant value 0·865 given by the other (heptyl to pentadecyl) members of the series. These variations from the constant for the series are difficult to explain, but will be further discussed in a paper with Dr. T. M. Lowry, who has made some very accurate determinations of the dispersive

* See Part V.

† Owing to the low rotatory power of the carbinol this value is probably not as accurate as the others given. There is, however, no doubt that the value of dispersive power (yellow/green) is much higher than that for the other members of the series.

powers of these carbinols at 20°, the results of which agree with those obtained by the present authors over the wide range of temperature employed.

Effect of Temperature on the Rotatory Powers.

The rotatory powers of the carbinols of the "ethyl" series are affected only very slightly by an increase of temperature, except in the case of methylethylcarbinol, which, although common to both the "methyl" and "ethyl" series, possesses physical constants abnormal to each. The effect of temperature on the rotatory powers is very much less in the "ethyl" than in the "methyl" and "isopropyl" series; so slight is this that it is difficult (considering the possibility of experimental error) to determine definitely any singular points in the temperature-rotation curves. Table II shows the values obtained from the smoothed curves at temperatures from 20° to 160°. There do not appear to be any obvious regularities in the temperature-rotation curves. Thus, for the propyl, butyl, and amyl members of the series, the molecular rotatory powers increase with the temperature up to the neighbourhood of their boiling points; for the hexyl, heptyl, and octyl members they increase to a maximum at about 120°, 80°, and 140° respectively; for the nonyl, decyl, and dodecyl members, the rotatory powers decrease as the temperature increases up to about 130°, and then fall as the temperature rises further, whilst for the undecyl, tridecyl, and pentadecyl members they decrease slowly as the temperature increases up to 160°. In nearly all these cases the variation in the molecular rotatory powers is not much larger than the possible experimental error in their determination. A comparison of the maximum values of the expression $[M]_D^{25}$ (as suggested by Patterson, this vol., p. 147) does not bring out any fresh regularities, at least between the limits $t^\circ = 20^\circ$ to 160° .

General Properties of the Optically Active Carbinols.

The members of the "ethyl" series of carbinols have not been described previously in the optically active form, except *d*-methylethylcarbinol, *d*- and *l*-ethylhexylcarbinol (see Part I., *loc. cit.*), and *d*-ethyl-*n*-amylcarbinol. The latter has been recently isolated in the laboratory of Messrs. Schimmel (Semi-Annual Reports, April, 1912, 103, and April, 1913, 82) from the by-products of low boiling point obtained in the rectification of menthol, and from this source had a rotatory power slightly lower than that of the synthetical carbinol now described.

These carbinols resemble those of the "methyl" and "isopropyl"

TABLE II.

Molecular Rotatory Powers for Sodium-yellow and Mercury-green Light and Dispersion Values of the Series $C_2H_5 \cdot CH(OH) \cdot R$ at Various Temperatures.

	At 20°.	40°.	60°.	80°.	100°.	120°.	140°.	160°.
<i>-Methylethylcarbinol</i>								
yellow	+10.02°	9.34°	8.73°	8.31°	—	—	—	—
green	11.91	11.05	10.31	9.82	—	—	—	—
disp.	0.842	0.845	0.847	0.846	—	—	—	—
<i>l-Ethyl-n-propylcarbinol</i>								
yellow	-2.01°	2.06°	2.12°	2.22°	2.32°	2.44°	—	—
green	2.29	2.34	2.42	2.54	2.64	2.75	—	—
disp.	0.881	0.881	0.877	0.875	0.882	0.887	—	—
<i>d-Ethyl-n-butylcarbinol</i>								
yellow	+9.43°	9.49°	9.58°	9.67°	9.78°	9.90°	10.06°	—
green	11.11	11.18	11.26	11.38	11.50	11.63	11.83	—
disp.	0.849	0.850	0.850	0.850	0.850	0.850	0.850	—
<i>d-Ethyl-n-amylcarbinol</i>								
yellow	+10.69°	10.82°	10.95°	11.06°	11.14°	11.21°	11.24°	11.22°
green	12.53	12.69	12.79	12.93	13.04	13.09	13.11	13.08
disp.	0.853	0.854	0.856	0.855	0.855	0.857	0.856	0.858
<i>l-Ethyl-n-hexylcarbinol</i>								
yellow	-10.63°	10.91°	11.10°	11.14°	11.15°	11.18°	11.04°	10.91°
green	12.43	12.72	12.86	12.93	12.96	13.00	12.90	12.77
disp.	0.856	0.858	0.863	0.861	0.860	0.859	0.856	0.854
<i>l-Ethyl-n-heptylcarbinol</i>								
yellow	-10.55°	10.64°	10.66°	10.70°	10.64°	10.54°	10.49°	10.38°
green	12.23	12.28	12.32	12.36	12.30	12.23	12.14	12.01
disp.	0.863	0.864	0.867	0.866	0.865	0.863	0.864	0.863
<i>l-Ethyl-n-octylcarbinol</i>								
yellow	-10.74°	10.86°	10.96°	10.99°	11.00°	11.00°	11.10°	10.91°
green	13.43	12.55	12.68	12.73	12.75	12.76	12.89	12.68
disp.	0.864	0.866	0.864	0.864	0.862	0.861	0.861	0.863

TABLE II. (continued).

<i>l</i> -Ethyl- <i>n</i> -nonylcarbinol	At 20°.	40°.	60°.	80°.	100°.	120°.	140°.	160°.
	* -11.09°	10.55°	10.33°	10.26°	10.21°	10.21°	10.33°	10.51°
	*12.86	12.25	11.91	11.80	11.76	11.81	11.90	12.12
disp.	0.863	0.862	0.867	0.869	0.868	0.864	0.868	0.868
<i>d</i> -Ethyl- <i>n</i> -decylcarbinol	* +12.44°	*12.35°	12.28°	12.20°	12.13°	12.11°	12.11°	12.17
	14.42	14.33	14.22	14.14	14.03	13.97	13.96	14.00
	0.862	0.862	0.863	0.863	0.865	0.867	0.868	0.869
<i>l</i> -Ethyl- <i>n</i> -undecylcarbinol	* -12.56°	*12.37°	12.28°	12.24°	12.19°	12.19°	12.16°	12.16°
	*14.55	*14.35	14.23	14.22	14.21	14.19	14.16	14.10
	0.863	0.862	0.863	0.861	0.858	0.858	0.859	0.862
<i>l</i> -Ethyl- <i>n</i> -dodecylcarbinol	* -12.61°	*12.41°	12.26°	12.15°	12.13°	12.10°	12.20°	12.36°
	*14.59	*14.32	14.15	14.07	14.04	14.02	14.12	14.30
	0.864	0.867	0.866	0.863	0.864	0.863	0.864	0.865
<i>l</i> -Ethyl- <i>n</i> -tridecylcarbinol	* -12.38°	*12.34°	*12.34°	12.25°	12.11°	11.97°	11.76°	11.57°
	*14.32	*14.35	*14.29	14.20	14.01	13.81	13.61	13.43
	0.865	0.861	0.863	0.862	0.864	0.866	0.862	0.864
<i>l</i> -Ethyl- <i>n</i> -pentadecylcarbinol	* -12.87°	*12.80°	*12.80°	12.79°	12.72°	12.71°	12.63°	12.31°
	*14.83	*14.80	*14.80	14.79	14.72	14.72	14.62	14.28
	0.868	0.865	0.865	0.865	0.864	0.863	0.864	0.863

* Values from extrapolated curves of densities and observed rotations. All values given in the table are read off or calculated from smoothed curves based on observations recorded on p. 1954.

series as regards immunity from "racemisation" * under many conditions (see Part II, *loc. cit.*, p. 622), whilst in general their physical properties (see table III) vary in a regular manner, except for the small breaks which occur in the regularity of the densities at the hexyl and dodecyl members (compare similar breaks in the "isopropyl" series and in the series of esters of *ac*-tetrahydro-2-naphthol, Parts II and III, *loc. cit.*).

The odours of the lower members of the series resemble those of the "methyl" series containing the same number of carbon atoms in the growing chain, the group R in the formulæ $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{R}$

TABLE III.

Optically Active Alcohols of the Formula $\text{C}_2\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{R}$.

	Boiling point.	Melting point.	n_D^{20} .†	D_{40}^{20} .	$\frac{n-1}{d} \cdot M$.	Mol. Refr. Differ- ence for CH_2 .	D_{40}^{80} .
Methylethylcarbinol ...	59°/758 mm.	—	1·3954	0·8080	36·2	7·7	—
Diethylcarbinol*	114·5°/752	„	1·4094	0·8198	43·9	7·5	—
Ethyl- <i>n</i> -propylcarbinol	133°/733	„	1·4141	0·8213	51·4	7·9	0·7671
Ethyl- <i>n</i> -butylcarbinol .	66°/18	„	1·4206	0·8227	59·3	7·7	0·7679
Ethyl- <i>n</i> -amylcarbinol .	76°/16	„	1·4252	0·8247	67·0	7·7	0·7711
Ethyl- <i>n</i> -hexylcarbinol .	97°/17	„	1·4308	0·8265	75·0	8·0	0·7796
Ethyl- <i>n</i> -heptylcarbinol	108°/15	„	1·4336	0·8272	82·9	7·9	0·7798
Ethyl- <i>n</i> -octylcarbinol..	117°/16	17°	1·4367	0·8295	90·6	7·7	0·7827
Ethyl- <i>n</i> -nonylcarbinol	130°/15	25	—	—	—	—	0·7833
Ethyl- <i>n</i> -decylcarbinol.	139°/12	32	—	—	—	—	0·7865
Ethyl- <i>n</i> -undecyl- carbinol	146°/10	38	—	—	—	—	0·7885
Ethyl- <i>n</i> -dodecyl- carbinol	168°/14	45	—	—	—	—	0·7921
Ethyl- <i>n</i> -tridecyl- carbinol	152°/4	50	—	—	—	—	0·7907
Ethyl- <i>n</i> -pentadecyl- carbinol	172°/2	56	—	—	—	—	0·7858

* Optically inactive.

† Determined with a Féry refractometer and correct to about $\pm 0\cdot0002$.

and $\text{C}_2\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{R}$ seemingly being the portion of the molecule to which the characteristic odour is due. Beyond the member with $\text{R} = n$ -decyl the odours are increasingly faint, ethyl-*n*-pentadecylcarbinol being practically odourless. No marked difference in odour between the optically active and inactive forms was observed in any case. The carbinols, when oxidised with chromic acid, readily yield in a pure state the ketones of the general formula $\text{C}_2\text{H}_5\cdot\text{CO}\cdot\text{R}$, which form semicarbazones in the usual way. The constants of these compounds are given in table IV, and differ

* It is very doubtful if any of these optically inactive carbinols exist in the liquid state as racemates (see investigations on the viscosity of several of these carbinols by Thole, this vol., p. 19).

in several instances from those previously recorded in the literature. The semicarbazones of the series $C_2H_5 \cdot CO \cdot R$ all crystallise readily from aqueous ethyl alcohol, but in the case of the higher members of the series melt at about the same temperature, and therefore, like the semicarbazones of the series $CH_3 \cdot CO \cdot R$, are of little use for the characterisation of the ketones.

TABLE IV.

Ketones of the General Formula $C_2H_5 \cdot CO \cdot R$.

Name of ketone.	Melting point.*	Boiling point.	Semicarbazone. Melting point.†
Ethyl methyl	—	78·6°	135—136°
Diethyl	—	101°	139
Ethyl <i>n</i> -propyl	—	123°	112°
Ethyl <i>n</i> -butyl	—	149—150°	99—100°
Ethyl <i>n</i> -amyl	—	165—166°	112°
Ethyl <i>n</i> -hexyl	—	185—186°	111°
Ethyl <i>n</i> -heptyl	—	211°	100—101°
Ethyl <i>n</i> -octyl	—	227°	89°
Ethyl <i>n</i> -nonyl	19°	134°/18 mm.	87°
Ethyl <i>n</i> -decyl	25°	140°/17 "	90°
Ethyl <i>n</i> -undecyl	33°	148°/10 "	89°
Ethyl <i>n</i> -dodecyl	38°	174°/20 "	90·5°
Ethyl <i>n</i> -tridecyl	40—41°	184°/17 "	86°
Ethyl <i>n</i> -pentadecyl.....	50°	198°/14 "	76°

* Determined by "cooling curve" method.

† These melting points, which were determined in a capillary tube, in several cases vary slightly according to the rate of heating. The figures given were obtained when the rate of heating was slow.

EXPERIMENTAL.

The experimental work has been carried out on similar lines to those described in Parts I to III. The externally compensated carbinols have been synthesised either by Grignard reactions or by the reduction of the corresponding ketones. The formation of a secondary alcohol by the interaction of a magnesium alkyl haloid and a normal aldehyde, $R \cdot CHO$, proceeds quite smoothly for aldehydes with R containing at least up to sixteen carbon atoms, but takes place only to a slight extent if the normal alkyl group is larger than *n*-propyl. The ketones were prepared (like those described in Parts I and II) by the catalytic decomposition (according to Senderens' method, *Compt. rend.*, 1909, **149**, 995) by contact with heated thorium oxide of mixtures of the required acids, these being, except where otherwise stated, the pure acids supplied by Kahlbaum. The thorium oxide was placed in a transparent silica "combustion" tube, the average yield from the process being apparently slightly better than when a Jena-glass tube is used, whilst the convenience in working is much greater.

It is noteworthy that, whilst the hydrogen phthalic esters of the "methyl" series are easily resolved by the fractional crystallisation of the brucine salts, the corresponding compounds of the "ethyl" series (like those of the *isopropyl* series) are in most cases more readily resolved by the aid of strychnine, as in several cases brucine appears to form a "partly racemic" salt, which is less soluble than either the *lB/A* or *lBdA* salt. The experimental results agree well with one another, so that it has not been thought necessary to publish the large mass of analytical details. Each stage of the processes described below has been checked by analysis, but all details, for example, of the titration of the acid esters with alkali, of the combustions of the semicarbazones, and of the alkaloidal salts, etc., and of the determination of the rotatory powers of the successive crops in the resolutions, have been omitted from the description. Both the dextro- and lævoro-rotatory forms of the carbinol have been obtained only in a few cases. The completeness of the resolutions has been to some extent assured by the following method. A quantity of the alkaloidal (generally strychnine) salt has been obtained with a rotation and melting point which remained unaltered by further recrystallisation. The mother liquors were then carefully worked up, and the salt thus obtained was subjected to another series of crystallisations. The resolution was deemed complete when the second lot of salt obtained in this manner had the same constants as the first lot. In each case as the strychnine salts are not always very definite compounds, the esters from each lot were prepared and examined separately in the polarimeter.

Preparation of the Hydrogen Phthalic Esters.

The hydrogen phthalic esters of the carbinols (see table V) were prepared by the following method. Equimolecular proportions of carbinol and phthalic anhydride are heated at 110—120° for about ten hours. The product is dissolved in very dilute sodium carbonate solution, and very carefully purified from non-acid substances by repeated extraction with ether. The solution, which when working up 100 grams of carbinol would amount to about 6 litres, is completely freed from dissolved ether by blowing a current of air through it for some hours. Then after the addition of an excess of hydrochloric acid the hydrogen phthalate is either drained off and dissolved in chloroform or at once extracted with that solvent. The chloroform solution is washed repeatedly with water, and carefully dried with recently fused calcium chloride, a process which removes all but mere traces of phthalic acid. The chloroform is then completely removed by distillation on a water-

bath, the last traces under diminished pressure, and the hydrogen phthalate (if solid) crystallised from petroleum of low boiling point. In most cases scrupulous adherence to these conditions is necessary to ensure the success of the subsequent resolution, which largely depends on the purity of the hydrogen phthalate.*

TABLE V.

The Hydrogen Phthalic Esters of the Carbinols, $C_2H_5 \cdot CH(OH) \cdot R$.

Hydrogen phthalate of carbinol with R=	Melting point of optically		Rotations in			
	Inactive.	Active.	Chloroform.		Ethyl alcohol.	
			$[\alpha]_D$.	$[M]_D$.	$[\alpha]_D$.	$[M]_D$.
<i>n</i> -Propyl	76–77°	73–74°	4·18°	10·45°	3·77°	9·42
<i>n</i> -Butyl	53–54	47–48	16·65	43·95	19·82	52·3
<i>n</i> -Amyl	62–63	66–68	17·06	59·7	21·67	60·2
<i>n</i> -Hexyl	47–49	54–55	14·12	41·2	19·45	56·8
<i>n</i> -Heptyl	Oil	32–33	12·67	38·8	17·30	52·9
<i>n</i> -Octyl	Oil	Oil	11·90	38·1	16·19	51·5
<i>n</i> -Nonyl	31–32	25	11·82	39·5	15·60	52·1
<i>n</i> -Decyl	46–47	34–35	12·84	44·7	17·71	61·6
<i>n</i> -Undecyl ...	58–60	36–37	13·79	49·9	17·43	63·1
<i>n</i> -Dodecyl ...	54–55	46–47	13·16	49·5	16·98	63·8
<i>n</i> -Tridecyl ...	51–52	51	12·55	49·0	16·47	63·2
<i>n</i> -Pentadecyl.	39–41*	31–35	12·16	50·8	15·62	65·3

* Not quite pure.

In all the determinations of the rotatory power of solutions recorded in this paper the material stated, usually about 1 gram, was made up to 20 c.c. at 20° with the solvent and the solution examined at 20° in a 2-dm. tube.

Methylethylcarbinol (sec.-Butyl Alcohol), $C_4H_{10}O$.

The preparation of *d*-sec.-butyl alcohol has been described briefly in Part I. Large quantities being required for this and other work, the methods have been modified as follows: Bright magnesium turnings (72 grams) are placed in a flask (capacity, 2 litres), and covered with ether† (250 c.c.). The flask is fitted with an inverted condenser, and a solution of dry ethyl bromide (340 grams), dissolved in an equal volume of ether, is added gradually, the mixture being shaken vigorously during the whole operation, which occupies about two hours. The flask is then placed in a large pneumatic trough standing on wooden rockers, and packed round with a mixture of ice and salt. A solution of acetaldehyde (150 grams) in twice its volume of ether is then slowly run in to

* It is thought desirable to emphasise this point as want of purity of the hydrogen phthalate appears to be the cause of failure on the part of some investigators to repeat resolutions previously described.

† Commercial ether which has been washed successively with concentrated sulphuric acid, water, a solution of sodium hydroxide and water, dried over calcium chloride, and distilled over phosphoric oxide.

the mixture from a tap funnel during the course of two hours, whilst the contents of the flask are agitated by moving the trough. The mixture is allowed to remain overnight, and then the uncombined acetaldehyde and about two-thirds of the ether are removed by distillation, the flask being placed in a bucket of water warmed to 45°. One operator can conveniently control simultaneously three series of such operations. The products from nine lots of material are poured with constant stirring into a large tank containing about 12 litres of a mixture of a saturated solution of ammonium chloride and crushed ice. The ethereal solution is then syphoned off, and the remaining liquid placed in flasks (capacity 5 litres), through which a current of steam is blown so long as the distillate smells of the alcohol. The distillates are collected together, and the alcohol concentrated by a repetition of the last operation. The ether in the syphoned liquid is removed by distillation, and the alcohol purified by distillation in a current of steam. The combined distillates are then saturated with sodium chloride, and extracted five times with ether. The ethereal extracts are now dried with several successive lots of recently ignited potassium carbonate, and then distilled very slowly through a long and efficient fractionating column. This last operation needs to be repeated four times, owing to the difficulty of separating ether and *sec.*-butyl alcohol. The average yield of the crude *sec.*-butyl alcohol (the fraction boiling between 85° and 101°) is well represented by that obtained from a batch of nine lots of material which amounted to 1265 grams.

The hydrogen phthalic ester is prepared by the method described on p. 1937, except that the mixture of the crude alcohol and phthalic anhydride is heated on a water-bath for about twelve hours. The amount of pure hydrogen phthalic ester obtained from the 1265 grams of crude alcohol mentioned above amounted to 3204 grams.

The resolution of methylethylcarbinol in large quantities is most easily carried out by a method which is illustrated by the details of one such resolution: The pure *sec.*-butyl hydrogen phthalate (965 grams) was dissolved in warm acetone (4 litres), and after the addition of anhydrous brucine (1738 grams), kept at about 40° for an hour. The solution was then filtered from undissolved brucine and concentrated, the flask being placed in a water-bath, and about 950 c.c. of acetone distilled off. After remaining for some hours in the ice-chest, the crop of crystals (*A*) was collected, whilst the filtrate (3000 c.c.) was concentrated further, and yielded another crop (*A*₁), the filtrate from which, when acidified in the manner described in Part I (p. 62), gave 260 grams of the hydrogen

phthalic ester with $[\alpha]_D - 20.0^\circ$ in ethyl alcohol. Crop *A* was recrystallised from 3 litres of acetone, giving crop *B* and the crop *A*₁ from the mother liquor of crop *B* giving crop *B*₁. Crop *B* was then recrystallised five times (crops *C*, *D*, *E*, *F*, *G*) from methyl alcohol, 1200 c.c. of solvent being used for each operation, since the solubility of salt decreases at about the same rate as the size of the crops; thus crop *D* weighed 1 kilo. and crop *G* 680 grams. Crop *B*₁ was then recrystallised successively from the mother liquors of crops *C* to *G*, and then a further six times from fresh methyl alcohol, the yield of salt being 180 grams. The total yield of salt (860 grams) was hydrolysed in the usual manner, and gave 276 grams of the pure *d*-sec.-butyl hydrogen phthalate,* with $[\alpha]_D + 38.44^\circ$ in ethyl alcohol. To obtain the alcohol from the ester the best procedure (giving a yield of 85 per cent.) is as follows: The ester (1 mol.) is dissolved in water containing sodium hydroxide ($2\frac{1}{2}$ mols.), the solution warmed for a few minutes, and the alcohol removed by a current of steam. The alcohol is separated after the addition of potassium carbonate to the distillate, and dried by treatment with successive lots of freshly-ignited potassium carbonate, and finally with barium oxide. It then boils constantly at $99^\circ/760$ mm., and has the rotation previously recorded (see Part I, 64).

Owing to the special interest attaching to this *d*-methylethyl-carbinol as the optically active alcohol of simplest constitution, further experiments were carried out to obtain the pure *l*-alcohol, so that other evidence as to the completeness of the resolution might be obtained.

The portions of ester of highest lævorotatory power (approximately $[\alpha]_D - 20^\circ$ in ethyl alcohol) were collected from several preparations of the *d*-alcohol, and converted into the acid potassium salt (see Part I, p. 59), which was then crystallised four times from acetone. This process did not alter the lævorotation of the ester, but the partly lævorotatory alcohol obtained from it was otherwise in a high state of purity. This was then converted into the hydrogen succinic ester, which gave a crystalline *cinchonidine* salt very soluble in organic solvents. This salt after five recrystallisations from a small quantity of acetone was obtained as small, transparent prisms melting at 54 — 55° , had $[\alpha]_D - 85.03^\circ$ in ethyl alcohol, and was unaltered in rotatory power after further recrystallisation. The *hydrogen succinic ester* obtained from this

* The rotation of this ester in chloroform, which is pure and recently distilled, is much higher ($[\alpha]_D + 40.54^\circ$) than the value ($[\alpha]_D + 33.54^\circ$) given in Part I. The rotations of this and other phthalic esters, when determined in chloroform solution, vary greatly with the purity of the solvent.

salt was a clear mobile oil, which had $[\alpha]_D -12.50^\circ$ in chloroform. When hydrolysed in the manner described for the corresponding *d*-hydrogen phthalic ester it gave the pure *l*-sec.-butyl alcohol, which in a 25 mm. tube had $\alpha_D^{22} -2.70^\circ$, the corresponding value obtained for the *d*-sec.-butyl alcohol in a 100 mm. tube being $\alpha_D^{22} -10.83^\circ$.

Methylethylcarbinol appears to have abnormal values for certain physical constants; thus, working with a sample of the *d*-alcohol prepared by us, Dunstan and Thole (compare this vol., p. 127) obtained abnormal values for log viscosity, whilst as recorded in Part II (p. 626) Dr. T. M. Lowry obtained a value for the optical dispersive power ($Hg_{\text{green}}^{\text{violet}} 1.662$) differing from the constant value (1.651) which he obtained for the other members of the "methyl" series. Suspicion having arisen that these anomalies might be due to the hygroscopic character of the alcohol and the presence of traces of water, the following experiments were carried out to test the point.

A series of polarimetric readings with the purest *d*-alcohol were made in a jacketed tube, through which warm water circulated. The successive readings in a 100 mm. tube were for $\alpha_{Hg \text{ green}}$ at 20° , $+13.02^\circ$; at 30° , 12.33° ; at 49° , $+11.29^\circ$; at 44° , $+11.55^\circ$; at 49° , $+11.28^\circ$; at 44° , $+11.60^\circ$; at 65° , $+10.51^\circ$; at 74° , $+10.27^\circ$; at 83° , $+9.90^\circ$; at 90° , $+9.70^\circ$; and at 96° , $+9.48^\circ$; whilst for α_D the readings taken at the same time were at 20° , $+10.94^\circ$; at 29° , $+10.46^\circ$; at 55° , $+9.31^\circ$; at 41.5° , $+9.88^\circ$; at 38° , $+10.01^\circ$; at 61° , $+9.04^\circ$; at 80° , $+8.46^\circ$; at 73.5° , $+8.68^\circ$; at 68° , $+8.93^\circ$; at 95° , $+8.12^\circ$; at 88° , $+8.26^\circ$. The values were plotted, and from the smoothed curves the following values of the dispersive power $\alpha_D/\alpha_{Hg \text{ green}}$ were obtained: at 20° , 0.842; at 40° , 0.845; at 60° , 0.847; at 80° , 0.846; at 90° , 0.846, the mean being 0.845. This sample was then allowed to remain for three days over barium oxide, and then re-examined in the polarimeter, with the result that all the new readings were found to lie on the curves previously obtained. One per cent. of water was next added to the sample, and the following readings obtained: for $\alpha_{Hg \text{ green}}$ at 19.5° , $+12.18^\circ$; at 30.5° , $+11.73^\circ$; at 35° , $+11.38^\circ$; at 47° , $+10.81^\circ$; at 59° , $+10.37^\circ$; at 66° , $+10.03^\circ$; at 78° , $+9.72^\circ$; at 82° , $+9.62^\circ$; at 86° , $+9.50^\circ$; for α_D at 19.5° , $+10.17^\circ$; at 44° , $+9.26^\circ$; at 38° , $+9.46^\circ$; at 91.5° , $+7.86^\circ$; at 81° , $+8.13^\circ$; at 72° , $+8.37^\circ$; at 63° , $+8.62^\circ$, whence the following values for the dispersive power were calculated; at 20° , 0.835; at 40° , 0.840; at 60° , 0.842; at 80° , 0.841; at 90° , 0.840, the mean value being 0.840. *sec*-Butyl alcohol appears to form with water a binary mixture, which boils at about 94° . The apparent

molecular weight of the alcohol in a 3 per cent. aqueous solution as measured by the depression of the freezing point was 75.8 (calculated 74). Equimolecular proportions of the alcohol and water are quite miscible; such a mixture when examined in the polarimeter in a 100 mm. tube gave $\alpha_D^{21} + 7.29^\circ$, $\alpha_{\text{Hg green}}^{21} + 8.66^\circ$, whence the dispersion value is 0.842. After three hours the polarimetric reading was $\alpha_{\text{Hg green}}^{19} + 8.75^\circ$, after five days $\alpha_D^{19} + 7.36^\circ$, after one month $\alpha_{\text{Hg green}}^{19.5} + 8.76^\circ$, $\alpha_{\text{Hg violet}}^{19.5} + 14.52^\circ$, whence the optical rotatory dispersion mercury violet/green is 1.657° . Further polarimetric readings of a pure sample of *d*-sec.-butyl alcohol gave, in a 2-dcm. tube, $\alpha_{\text{violet}}^{20} + 42.26^\circ$ and $\alpha_{\text{violet}}^{21} + 25.52^\circ$, whence the rotatory dispersion is 1.656. It therefore seems certain that the value of the rotatory optical dispersion of sec.-butyl alcohol, although different from the normal values shown by other members of both the "methyl" and "ethyl" series, is not appreciably affected by traces of water.

Ethyl-n-propylcarbinol, $\text{C}_6\text{H}_{14}\text{O}$.

The crude carbinol was prepared in the usual manner by the interaction of magnesium *n*-propyl chloride and propaldehyde. The yield from twice the gram-molecular quantities was 62 grams of the crude alcohol boiling at $130\text{--}140^\circ$.

Resolution.—The optically inactive hydrogen phthalic ester (97 grams) in the form of the hard rhombs (m. p. $76\text{--}77^\circ$), in which it crystallises from light petroleum, was dissolved in acetone (about 2 litres), and the solution heated to about 40° for half-an-hour with brucine (153 grams), filtered, concentrated to about 500 c.c., and allowed to remain overnight in the ice-chest. The crystalline salt was then collected, and the process of crystallisation repeated several times, increasingly smaller amounts of solvent being employed. After four more such crystallisations, 52 grams of the brucine salt were obtained in hard and transparent, prismatic rods, melting at $132\text{--}133^\circ$, and with $[\alpha]_D - 8.92^\circ$ in ethyl alcohol. To this salt were added a further 23 grams (with $[\alpha]_D - 8.70^\circ$), obtained by working up all, but the first, mother liquors in the manner described for the strychnine salts of the dextrorotatory hydrogen phthalates of ethyl- and *n*-amyl-isopropylcarbinols (Part II, p. 632), six crystallisations being carried out and fresh solvent employed for the last three. These 75 grams were once more recrystallised from acetone, and the salt with $[\alpha]_D - 8.91^\circ$ decomposed in the usual manner (see Part I, p. 61). The levorotatory hydrogen phthalic ester (26 grams) crystallised from light petroleum in small, prismatic needles, melted at $73\text{--}74^\circ$, and had $[\alpha]_D - 4.12^\circ$ in chloroform and $[\alpha]_D - 3.75^\circ$ in ethyl alcohol. The pure ester (22 grams) was dissolved in a hot aqueous solution of

potassium hydroxide (14 grams), and the *l*-ethyl-*n*-propylcarbinol removed by a current of steam. After extraction with ether in the usual manner, there were obtained 7.7 grams, boiling at 133—134°/733 mm. The first mother liquor from the crystallisation of the brucine salt was decomposed, and the ester (18 grams) with $[\alpha]_D + 2.3^\circ$ in ethyl alcohol converted into the strychnine salt in the usual manner (Part II, p. 632), chloroform and ethyl alcohol being the solvents employed. After five crystallisations the pure *strychnine* salt (11 grams) was obtained. The salt melted at 191—192°, had $[\alpha]_D - 21.26^\circ$ in chloroform, and, when decomposed in the usual manner, yielded the pure dextrorotatory *ester*, which, when crystallised from light petroleum, melted at 73—74° and had $[\alpha]_D + 4.18^\circ$ in chloroform and $[\alpha]_D + 3.77^\circ$ in ethyl alcohol. Equal amounts of the *d*- and *l*-esters were dissolved in light petroleum, and the solution seeded with the optically inactive ester, when the resulting crop of crystals melted at 75—76°. The *d*-carbinol boiled at 133—134°/733 mm., and in a 25 mm. tube gave $\alpha_D^{18} + 0.45^\circ$. The carbinol, recovered from the esters with lower rotations, was oxidised by warming gently with a solution of chromic acid, and yielded ethyl *n*-propyl ketone. This boiled at 122—124°, and formed a semicarbazone, which separates from ethyl alcohol in long, prismatic needles, and melts at 112°.

Ethyl-n-butylcarbinol, $C_7H_{16}O$.

The material required for the preparation of the optically active carbinol was obtained by the reduction of the corresponding ketone. The latter was prepared by passing a mixture of *n*-valeric (150 grams) and propionic (450 grams) acids through a silica tube heated to 400° and containing thorium oxide. The unchanged acids were collected and passed through the tube again, the total yield of crude ketone boiling at 147—148° being 105 grams. This ethyl *n*-butyl ketone was reduced in moist ethereal solution by finely-divided sodium, and gave 95 grams of the crude ethyl-*n*-butylcarbinol boiling at 150—152°. This carbinol, when treated with phthalic anhydride, gave 173 grams of the hydrogen phthalic ester, which crystallises from light petroleum in slender needles melting at 53—54°. This ester (151 grams) was converted into the *strychnine* salt by heating its solution in methyl alcohol with the alkaloid (190 grams). The pure salt crystallises in hard, lustrous prisms, melts at 176°, and has $[\alpha]_D - 24.31^\circ$ in chloroform. The first five crystallisations from fresh lots of methyl alcohol gave 9.5 grams of the pure salt, whilst the second crop from the second mother liquor was recrystallised from the succeeding three filtrates and four more times from fresh lots of solvent,

yielding a further 10 grams of the salt. The *esters* obtained from the crops of pure salt weighed 4.5 and 3.5 grams respectively, and had $[\alpha]_D + 16.53^\circ$ and $+ 16.65^\circ$ in chloroform. The resolution was repeated with 82 grams of the inactive ester, and 9 grams of the active ester (with $[\alpha]_D + 16.24^\circ$ in chloroform) obtained. The *hydrogen phthalic* ester of *d*-ethyl-*n*-butylcarbinol crystallises readily from light petroleum in lustrous, prismatic needles, melts at $47-48^\circ$, has $[\alpha]_D + 19.82^\circ$ in ethyl alcohol, and is easily hydrolysed by potassium hydroxide. The dextrorotatory carbinol was isolated in the usual manner, and boiled at $66^\circ/18$ mm. The strychnine salts of the *d*- and *l*-esters do not vary very widely in solubility in methyl alcohol, the first mother liquor in the first resolution described above giving an ester only having $[\alpha]_D - 2.0^\circ$ in chloroform. Two series of experiments were carried out, in which strongly dextrorotatory and levorotatory hydrogen phthalic esters were converted into the corresponding brucine salts. When either lot of brucine salt was recrystallised several times from acetone it was found that the least soluble portion in each case gave an ester, which was optically inactive. It thus appears that brucine forms a partly racemic salt with the hydrogen phthalic ester of ethyl-*n*-butylcarbinol.

Ethyl-n-amylcarbinol, $C_8H_{18}O$.

The optically inactive carbinol was prepared in a similar manner to that described for the corresponding *n*-butyl compound. A mixture of 145 grams of *n*-hexoic and 180 grams of propionic acids gave 124 grams of crude ethyl *n*-amyl ketone boiling between 160° and 170° . From this, 106 grams of the crude carbinol boiling at $168-172^\circ/753$ mm. were obtained and 197 grams of the corresponding hydrogen phthalic ester.

The resolution of the hydrogen phthalic ester of ethyl-*n*-amylcarbinol by the fractional crystallisation of the strychnine salt from methyl alcohol proceeds fairly readily. The ester (137 grams), which had been obtained from light petroleum in large, transparent plates melting at $62-63^\circ$, was dissolved in $1\frac{1}{2}$ litres of methyl alcohol, in which the strychnine (164 grams) was suspended. The resolution was carried out as in the case of ethyl-*n*-butylcarbinol. The pure *strychnine* salt of the *d*-ester, obtained after seven crystallisations, melted (when heated slowly) at $164-166^\circ$, and had $[\alpha]_D - 24.41^\circ$ in chloroform. Systematic working up of the filtrate (fourteen further crystallisations) gave more of the salt, which with the former lot yielded 16.5 grams of the pure *d*-ester. This crystallised from light petroleum in hard, vitreous plates, melted at $66-68^\circ$, and had $[\alpha]_D + 16.96^\circ$ in

chloroform and $[\alpha] + 21.67^\circ$ in ethyl alcohol. The *d*-carbinol obtained in the usual manner boiled at $76^\circ/16$ mm. The *l*-ester recovered from the first mother liquor had $[\alpha]_D - 7.0^\circ$ in chloroform, but neither from this nor from the optically inactive ester could the pure *l*-ester be obtained by ten crystallisations of the brucine salt from acetone. This alkaloid forms a stable partly racemic salt, which softens at $102\text{--}107^\circ$, melts at $121\text{--}123^\circ$, has $[\alpha]_D - 9.01^\circ$ in ethyl alcohol, and when decomposed yields the inactive ester melting at $61\text{--}63^\circ$.

Ethyl-n-hexylcarbinol, $C_9H_{20}O$.

The resolution of this carbinol has been already described in Part I (*loc. cit.*). It has been repeated, using a hydrogen phthalic ester, which was prepared from a sample of the carbinol obtained by the reduction of the corresponding ketone. Analogous results were obtained, various lots of ester from the pure brucine, *strychnine* and *cinchonidine* salts having respectively $[\alpha]_D + 14.03^\circ$, $+14.12^\circ$, and -13.73° in chloroform.* The strychnine salt crystallises from methyl alcohol in prisms, melts at $146\text{--}147^\circ$, and has $[\alpha] - 23.41^\circ$. The carbinols obtained from these different lots of esters had rotatory powers identical with those previously described (*loc. cit.*).

Ethyl-n-heptylcarbinol, $C_{10}H_{22}O$.

Ethyl n-heptyl ketone, $C_{10}H_{20}O$, is readily prepared by the Senderens catalytic process. A mixture of *n*-octoic (200 grams) and propionic (400 grams) acids passed twice over thoria heated to 400° gave 146 grams of the ketone, which boiled at 211° . It is much more readily reduced by sodium in moist ethereal solution than in moist ethyl-alcoholic solution. From the above quantity of ketone 130 grams of the corresponding *ethyl-n-heptylcarbinol*, boiling at 213° , were obtained. The oily *hydrogen phthalic* ester of this could not be made to crystallise even when cooled to a low temperature, and seeded with a speck of the *laevorotatory* form described below. It is readily resolved by means of strychnine, the details of one experiment being as follows: The ester (157 grams) and strychnine (171 grams) were dissolved in chloroform, which was then removed as completely as possible on a water-bath, the resulting paste being rapidly dissolved in acetone (1 litre) previously heated to its boiling point. The crop (*A*) of crystals (m. p. $119\text{--}122^\circ$) deposited when this solution cooled was recrystal-

* The esters described in Part I (*loc. cit.*) had $[\alpha]_D + 13.78^\circ$ and -13.62° in chloroform. An obvious miscalculation of the molecular rotatory powers recorded in Part I, table IX, is corrected in table V of this paper (see p. 1938).

lised by a similar process, giving crop *B*, which was then recrystallised eight times from fresh lots of methyl alcohol, 72 grams of the pure *strychnine* salt of the *l*-ester being obtained. The salt melts at 140—141°, and has $[\alpha]_D -18.18^\circ$ in pure chloroform. The mother liquors from crops *A* and *B* were decomposed, and gave respectively 52 grams and 19 grams of ester with $[\alpha]_D +6.4^\circ$ and $+4.2^\circ$ in pure chloroform. The 72 grams of the above-mentioned salt and a further small amount obtained by systematically working up the alcoholic mother liquors gave 25 grams of the *l*-ester, which solidified on cooling to a fairly hard, crystalline mass. This was pressed out on a porous tile, when it melted at 32—33°, and had $[\alpha]_D -17.30^\circ$ in ethyl alcohol and -12.67° in chloroform. Samples of the ester with $[\alpha]_D$ in chloroform about $+5^\circ$ and -3° respectively formed brucine salts, which crystallised readily from acetone. Each lot when crystallised repeatedly from acetone gave the same (partly racemic) *brucine* salt, which melted at 112—114°, had $[\alpha]_D -7.46^\circ$ in ethyl alcohol, and from which an optically inactive and oily ester was obtained. *l*-Ethyl-*n*-heptylcarbinol is readily obtained by the hydrolysis of the *l*-ester in the usual manner, is volatile in a current of steam, and boils at 108°/15 mm.

Ethyl-n-octylcarbinol, $C_{11}H_{24}O$.

Two separate mixtures of *n*-nonoic (150 grams) and propionic (460 grams) acids when treated by the Senderens process, gave yields of *ethyl n-octyl ketone*, $C_{11}H_{22}O$, amounting to 108 and 105 grams respectively. This crude ketone boiled at 223—228°, and was not readily reduced by sodium in boiling ethyl alcohol. Thus, 105 grams of the ketone, when reduced by these means in the usual manner, only gave 50 grams of crude ethyl-*n*-octylcarbinol, which boiled at 225—230°, and was readily converted into the oily *hydrogen phthalic* ester. This was easily resolved by the aid of strychnine. A mixture of the ester (116 grams) and strychnine (122 grams) was dissolved in boiling methyl alcohol, and the crude salt obtained from this solution crystallised six times from fresh amounts of the solvent. The melting point (142—143°) and the rotatory power ($[\alpha]_D -16.75^\circ$ in chloroform) of the strychnine salt thus obtained were unaltered by three further recrystallisations. The oily *l*-ester from the salt thus purified amounted to 16.5 grams, and had $[\alpha]_D +16.10^\circ$ in ethyl alcohol, and $[\alpha]_D -11.90^\circ$ in chloroform. *l*-Ethyl-*n*-octylcarbinol is volatile with steam, boils at 117°/16 mm., and when cooled sets to a mass of crystalline needles, which melt at 17°. Samples of the ester having low dextro- and lævo-rotatory powers formed brucine salts, which were very soluble in acetone. These salts, after several recrystallisations, became less

soluble, and yielded specimens of ester which were almost optically inactive. An ester of very low rotatory power yielded a carbinol, which boiled at 229°.

Ethyl-n-nonylcarbinol, $C_{12}H_{26}O$.

Ethyl-*n*-nonylcarbinol was prepared by the action of magnesium ethyl bromide on *n*-decaldehyde. The required aldehyde was obtained by the general method discovered independently by Le Sueur (T., 1904, **85**, 827) and Blaise (*Compt. rend.*, 1904, **138**, 697). Three hundred grams of *n*-undecic acid* were brominated with 516 grams of bromine and red phosphorus in the usual manner, 342 grams of α -bromo-*n*-undecic acid, $C_{11}H_{21}O_2Br$, boiling at 178–183°/14 mm., and melting at 10°, being obtained.† The bromo-acid (776 grams) was dissolved in $6\frac{3}{4}$ litres of water, $1\frac{1}{2}$ kilos. of commercial sodium hydroxide were added, and a rapid current of superheated steam was blown for twenty hours through the mixture, which was placed in a large and deep earthenware vessel (an ordinary domestic "bread mug"). After acidification, the solid obtained was crystallised from light petroleum, and gave 570 grams of the pure α -hydroxy-*n*-undecic acid, $C_{11}H_{22}O_3$, which melts at 74°. The hydroxy-acid was rapidly distilled in portions of 15 grams from small flasks under ordinary pressure, and the products redistilled under diminished pressure, the whole series of operations being repeated with the portions boiling above 110°/14 mm. In this manner 88 grams of *n*-decaldehyde (b. p. 98°/13 mm.) were obtained from 240 grams of the hydroxy-acid. The freshly distilled aldehyde (88 grams) was then added in the

* *Preparation of undecic acid.*—A large quantity of *n*-undecic acid was prepared for the synthesis of ethyl-*n*-nonyl- and ethyl-*n*-decyl-carbinols. The details of the preparation are as follows: The slow distillation under 40 mm. pressure of 18 kilos. of crude castor oil in half-kilo. lots gave, after careful fractionation of the products, 1180 grams of *n*-undecenoic acid and 1605 grams of *n*-heptaldehyde. The acid was esterified by the Fischer—Speier method (*Ber.*, 1895, **28**, 3252), using 4540 grams of 96 per cent. ethyl alcohol and 394 grams of concentrated sulphuric acid. After careful fractionation 1162 grams of ethyl *n*-undecenoate were obtained and reduced catalytically in an atmosphere of hydrogen in the presence of finely divided nickel heated to 170° (Darzens, *Compt. rend.*, 1907, **144**, 329). The ester was passed four times over the nickel (the refraction being practically unaltered by the fourth operation), was then well shaken with one per cent. solution of potassium permanganate, dried in the usual way and again carefully fractionated, 975 grams of ethyl undecate (b. p. 140°/20 mm.) being obtained. When hydrolysed, the yield of undecic acid, which melted sharply at 28° and boiled at 179°/28 mm., amounted to 774 grams. Further quantities of this acid were prepared in a similar manner from undecenoic acid obtained from Kahlbaum.

† In a second preparation, 434 grams of the bromo-acid were obtained from 346 grams of *n*-undecic acid.

usual manner to a slight excess of magnesium ethyl bromide, and gave 85 grams of *ethyl-n-nonylcarbinol*, which boils at $133^{\circ}/14$ mm., and when cooled sets to a gelatinous, microcrystalline mass, melting at 12° . From this amount of carbinol were obtained 126 grams of the *hydrogen phthalic* ester, which after some days in the ice-chest set to a hard, crystalline mass, melting at $31-32^{\circ}$. It is readily resolved by the fractional crystallisation of the strychnine salt from methyl alcohol. The yield from equal quantities (123 grams) of the racemic ester and strychnine, after eight crystallisations of the salt of the pure *l*-ester, amounted to 18 grams. Further quantities of the salt were obtained from the mother liquors, twenty-one crystallisations being carried out. The *strychnine* salt of the *l*-ester melts at $129-130^{\circ}$, and has $[\alpha]_D -16.12^{\circ}$ in chloroform. The *l*-ester, of which in all 16 grams were obtained, solidifies in rosettes of needles, which melt at 25° , and has $[\alpha]_D -15.60^{\circ}$ in ethyl alcohol and $[\alpha]_D -11.82^{\circ}$ in chloroform. *l*-*Ethyl-n-nonylcarbinol* is volatile in a current of steam, boils at $130^{\circ}/15$ mm., and sets to a hard, crystalline mass, which melts at 25° . The odour of the carbinol is very similar to that of methyl-nonylcarbinol (and ketone).

Ethyl-n-decylcarbinol, $C_{13}H_{28}O$.

A mixture of 156 grams of *n*-undecic acid,* with 220 grams of propionic acid, passed over thoria, heated to 420° , gave 109 grams of *ethyl n-decyl ketone*, $C_{13}H_{26}O$,† which boils at $140^{\circ}/17$ mm., sets to a mass of pearly plates melting at 25° , and has only a very faint odour. In boiling *isoamyl* alcohol, it is reduced by sodium to the corresponding *carbinol* (yield, 72 per cent.), which boils at $148^{\circ}/20$ mm., solidifies in the ice-chest to a waxy mass of platelets, and melts at 14.5° . The racemic *hydrogen phthalic* ester is very soluble in light petroleum, melts at $46-47^{\circ}$, and can be resolved by the fractional crystallisation of the strychnine salt from methyl alcohol. The resolution was carried out twice, most perplexing results being obtained, as the least soluble strychnine salts separating out at different stages appeared to correspond in an erratic manner with both that of the *l*-ester and that of the *d*-ester. The resolution was then repeated a third time, care being taken to carry out each crystallisation under similar conditions as to temperature, the details of the crops being as follows: 117 grams of the racemic ester and 114 grams of strychnine were dissolved in half a litre of methyl alcohol, the crystals (crop *A*) which separated out being recrystallised six times (crops *B* to *G*), each

* Completely free from undecenoic acid.

† A second preparation gave 96 grams of the ketone from a mixture of 128 and 300 grams of respective acids.

time from about 100 to 150 c.c. of the solvent. Crop *E* weighed 16 grams, and melted at 131—132°; crop *F*, weighing 13 grams, was identical with crop *G* as regards melting point (132°) and rotatory power ($[\alpha]_D - 24.80^\circ$ in chloroform), and was the pure *strychnine* salt of the *d*-ester.* The mother liquor from crop *A* was concentrated, and crop *B*₁, amounting to 55 grams, obtained. Crop *B*₁ was recrystallised from the mother liquor of crop *C*, the crystals, crop *C*₁, amounting to 35 grams. In a similar manner crops *D*₁, *E*₁, *F*₁ were obtained, *F*₁ † being then recrystallised five times from fresh lots of solvent, giving crops *G*₁, *H*₁, *K*₁, *L*₁, and *M*₁. The crystals of crop *M*₁, which amounted to 9 grams, when heated very slowly, melted at 119—120°, had $[\alpha]_D - 14.58^\circ$ in chloroform, and consisted of the *strychnine* salt of the *l*-ester.‡ The remaining liquors were decomposed, details relating to the respective esters obtained from them being given in table VI.

TABLE VI.

Resolution of the Hydrogen Phthalic Ester of Ethyl-n-decylcarbinol.

Weight of ester (in grams).	derived from the mother liquor of crop	Rotation $[\alpha]_D$, in chloroform.*
23.0	<i>A</i>	-2.6°
36.0	<i>B</i> ₁	+0.8
13.0	<i>C</i> ₁	+3.4
5.0	<i>D</i> ₁	+2.6
11.0	<i>E</i> ₁	+1.4
2.0	<i>F</i> ₁	+3.1
3.0	<i>G</i> ₁	-3.6
2.5	<i>H</i> ₁	-8.1
1.0	<i>K</i> ₁	-9.9
0.5	<i>L</i> ₁	-11.9
0.5	<i>M</i> ₁	-13.1

* Not specially purified. The same sample of chloroform was used for each of the determinations recorded.

The *d*- and *l*-esters obtained from the corresponding pure *strychnine* salts (crop *G* to the *d*-ester and crop *M*₁ to the *l*-ester) solidified after evaporation of their solutions in ether to hard, crystalline masses, each of which melted at 35—35.5°. Determinations of the rotatory power gave the following results: For the *d*-ester, $[\alpha]_D + 12.84^\circ$ and $+ 17.58^\circ$; for the *l*-ester, $[\alpha]_D - 12.83^\circ$ and $- 17.71^\circ$; the determinations in each case being in chloroform and ethyl alcohol respectively.

0.1 Gram of both esters was separately and accurately weighed out, mixed, and dissolved in pure chloroform. After evaporation of the solvent, the resulting hard, crystalline mass melted sharply

* *Sic.*

† The mother liquor from the crop *G* was decomposed along with crop *H* to obtain the *d*-ester.

‡ *Sic.*

at 46°, that being the melting point of the racemic ester previously obtained.* The optically active forms of *ethyl-n-decylcarbinol* are volatile in a current of steam, and each melts at 32°. Approximately equal amounts of each were mixed together on a porous tile, when the mixture rapidly fused, and was absorbed by the tile, the temperature of the room being 17°, and the melting point of the racemic carbinol 14.5°. The *d*-carbinol (from the *d*-ester) boiled at 139°/12 mm., and the *l*-carbinol at 140°/15 mm., each crystallising from ethyl alcohol in long and slender, silky needles.

Ethyl-n-undecylcarbinol, $C_{14}H_{30}O$.

Ethyl n-undecyl ketone, $C_{14}H_{28}O$, is readily prepared by passing a mixture of equal amounts of lauric and propionic acids over thorium oxide heated to 425°, the yield being just over 60 per cent. of the lauric acid employed. It boils at 148°/10 mm., solidifies in nacreous plates, melts at 33° (compare Blaise and Guérin (*Bull. Soc. chim.*, 1903, [iii], **29**, 1208), and when dissolved in boiling amyl alcohol, is reduced by sodium to the corresponding

* Another remarkable case which in some respects is possibly analogous to the uncommon phenomena just described has been investigated in these laboratories. Pope and Read (T., 1912, **101**, 758) have described the externally compensated and optically active hydroxyhydrindamines, recommending the latter as serviceable bases for the resolution of externally compensated acids. With the kind concurrence of Prof. W. J. Pope we have prepared and resolved a large quantity of the externally compensated hydroxyhydrindamine, following the directions given in the above-mentioned paper. However, as we had available the ammonium salt of only *d*- α -bromocamphor- π -sulphonate we expected to be able to prepare only the *l*-hydroxyhydrindamine as Pope and Read obtained the *l*BdA-salt as the least soluble component of the mixture formed by addition of an aqueous solution of ammonium *d*- α -bromocamphor- π -sulphonate (1 mol.) to an aqueous solution of *dl*-hydroxyhydrindamine hydrochloride (2 mols.). To our surprise, however, we obtained instead the *d*BdA-salt, from which was obtained the pure *d*-hydroxyhydrindamine with $[\alpha]_D + 22.8^\circ$ in water as described by Pope and Read. Our colleague, Mr. Yates, then carefully repeated the resolution, not only as described by Pope and Read, but also under varied conditions of temperature and concentration, and used throughout the ammonium salt of the dextrorotatory acid only. In each case the salt separating out was the *d*BdA-isomeride (m. p. 152°). Prof. Pope then very kindly forwarded a small specimen of the *l*BdA-salt (m. p. 221°). Following then the directions of Pope and Read, the accumulation of partially *l*-hydroxyhydrindamine hydrochloride was (by use of the seed) converted into the *l*BdA-salt by the double decomposition of the hydrochloride and the ammonium *d*- α -bromocamphor- π -sulphonate in the required proportions calculated from the rotatory power of the hydrochloride. In this way a good yield of both the dextrorotatory and *l*-hydroxyhydrindamine was obtained from the resolution, the ammonium salt of the dextrorotatory acid only being employed. These bases appear to have no advantage over the commoner alkaloids for use in the resolution of externally compensated hydrogen phthalic or succinic esters.

ethyl-n-undecylcarbinol (yield, 80 per cent.), which boils at $173^{\circ}/25$ mm., solidifies in stellate masses of long needles with a pearly lustre, and melts at 25° . The *hydrogen phthalic* ester of the carbinol crystallises from light petroleum, and melts at $58-60^{\circ}$. The resolution of this ester by the fractional crystallisation of the strychnine salts from methyl alcohol was carried out in a manner as described for similar compounds. Thus, 158 grams of the ester and 145 grams of strychnine were dissolved in methyl alcohol, and the crop of crystals (160 grams) deposited when the solution was cooled was recrystallised six times, there being obtained 37 grams of the *strychnine* salt of pure *l*-ester, which crystallises from methyl alcohol in clear, transparent prisms, melts at $100-101^{\circ}$, and has $[\alpha]_D -13.96^{\circ}$ in chloroform. The mother liquors were systematically worked up as usual, the product obtained after three recrystallisations from fresh solvent having identical properties with those of the main lot (37 grams) of the pure salt. The *l-hydrogen phthalic* ester is very soluble in light petroleum, from which it crystallises in feathery needles, melts at 33° , and has $[\alpha]_D -13.79^{\circ}$ and -17.43° in chloroform and ethyl alcohol respectively. *l-Ethyl-n-undecylcarbinol* is only very slowly volatile in a current of steam, boils at $146^{\circ}/10$ mm. or $160^{\circ}/15$ mm., sets on cooling to a hard, crystalline mass, can be recrystallised from ethyl alcohol, from which it separates in stout prisms, and melts at 38° .

Ethyl-n-dodecylcarbinol, $C_{15}H_{32}O$.

This carbinol was prepared by interaction of magnesium ethyl bromide and *n*-tridecaldehyde. The required aldehyde was prepared by Le Sueur's method (*loc. cit.*), but the yields were poor, as from 240 grams of pure α -hydroxymyristic acid only 62 grams of the pure aldehyde were obtained. The Grignard reaction proceeds quite smoothly, in two separate experiments the yields obtained of the carefully fractionated carbinol being 36 and 14 grams from 48 and 14 grams respectively of the aldehyde. *Ethyl-n-dodecylcarbinol* boils at $163^{\circ}/12$ mm., and sets on cooling to an opaque, crystalline mass, which melts at 32° . Seventy-three grams of the pure racemic *hydrogen phthalic* ester were obtained from 50 grams of the racemic carbinol. The ester crystallises from light petroleum, and melts at $54-55^{\circ}$. The resolution of the ester by the fractional crystallisation of the strychnine salt from methyl alcohol proceeded with unusual rapidity. Seventy-three grams of the ester and 65 grams of strychnine were dissolved in methyl alcohol (100 c.c.). After cooling, 82 grams of crystals were deposited, whilst the ester obtained from the mother liquor had $[\alpha]_D +9.3^{\circ}$ in chloroform. After three recrystallisations of

these crystals, the *strychnine* salt of the pure *l*-ester was obtained. This salt, which was unaltered by three further recrystallisations, melted at 103—104°, and had $[\alpha]_D -12.45^\circ$ in chloroform. The *l*-ester (20 grams) obtained from the salt crystallised from light petroleum, melted at 46—47°, and had $[\alpha]_D -13.16^\circ$ and -16.98° in chloroform and ethyl alcohol respectively. *l*-Ethyl-*n*-dodecylcarbinol is not volatile in a current of steam, boils at 168°/14 mm., sets on cooling to a hard, crystalline mass, separates from ethyl alcohol in long, silky needles, melts at 45°, and has no odour.

Ethyl n-dodecyl ketone, $C_{15}H_{30}O$, was prepared by the oxidation of the carbinol with chromic acid, and is slowly volatile in a current of steam. Thus purified, it is obtained in large, glistening plates, which melt at 38°.

Ethyl-n-tridecylcarbinol, $C_{16}H_{34}O$.

A mixture of equal amounts of myristic and propionic acids passed over thoria heated to 420° gave a 60 per cent. yield of *ethyl n-tridecyl ketone*, $C_{16}H_{32}O$, which boils at 184°/17 mm., and crystallises from light petroleum in lustrous leaflets, melting at 42°. When reduced by sodium in boiling *isoamyl* alcohol, it gave the corresponding *carbinol*, which boils at 176°/16 mm., and on cooling sets to a hard, crystalline mass, melting at 37—38°. The *hydrogen phthalic* ester separates from light petroleum in clusters of silky needles, and melts at 51—52°.

The resolution of the ester was carried out in the usual manner by the fractional crystallisation of the *strychnine* salt from acetone containing a small amount of chloroform. A mixture of the ester (126 grams) and *strychnine* (108 grams) was dissolved in chloroform, which was then removed as completely as possible by distillation on a water-bath, the resulting paste being quickly dissolved in warm acetone. The crystals deposited from this solution weighed 67 grams, and were recrystallised six times in a similar manner, 27 grams of the *strychnine* salt of the pure *l*-ester being obtained. After recrystallisation of the products given by systematically working up the mother liquors, a further quantity of the pure salt was obtained, the *l*-ester from both lots of salt amounting to 26 grams. The *strychnine* salt of the *l*-ester crystallises from acetone in stout, glassy rods, melts at 103—104° and has $[\alpha]_D -14.66^\circ$ in pure chloroform. The *l*-ester crystallises from light petroleum in prismatic needles, melts at 51°, and has $[\alpha]_D -12.55^\circ$ and -16.47° in pure chloroform and ethyl alcohol respectively. *l*-Ethyl-*n*-tridecylcarbinol is not readily volatile in a current of steam, it boils at 152°/4 mm., melts at 50°, separates

from ethyl alcohol in rosettes of very slender needles, and is almost odourless.

Ethyl-n-pentadecylcarbinol, $C_{18}H_{38}O$.

A warm solution of palmitic acid (300 grams) in propionic acid (400 grams) was passed over thoria heated to 430° , and 114 grams of *ethyl n-pentadecyl ketone*, $C_{18}H_{36}O$, were obtained, 102 grams of pure palmitic acid being recovered. The ketone boils at $198^{\circ}/14$ mm., and sets on cooling to a crystalline mass, melting at 50° . When reduced in boiling *isoamyl* alcohol by means of sodium, the corresponding *carbinol* is formed, the yield being 70 per cent. This boils at $202^{\circ}/13$ mm., and melts at 43° . The *hydrogen phthalic* ester, as prepared in the usual manner, melted at $39-41^{\circ}$, but was probably not quite pure, as the solutions of the sodium salt are of a soapy character and difficult to extract with ether. The resolution of the ester was carried out by an analogous method to those described above. The ester (118 grams) and strychnine (80 grams) were dissolved in methyl alcohol, the solution concentrated, and allowed to remain in the ice-chest. The crop of crystals obtained melted at $84-87^{\circ}$, and was recrystallised six times from methyl alcohol, the final crop weighing 30 grams, and melting at $108-109^{\circ}$. The *strychnine* salt of the *l-ester* had $[\alpha]_D -12.57^{\circ}$ in chloroform, a further quantity being obtained from a systematic working up of the mother liquors (five operations), and recrystallising the product three times from fresh solvent. From both lots of the salt 19.5 grams of the *l-ester* were obtained; it melts at $32-33^{\circ}$, and has $[\alpha]_D -15.62^{\circ}$ and -12.16° in ethyl alcohol and chloroform respectively. *l-Ethyl-n-pentadecylcarbinol* boils at $172^{\circ}/2$ mm., melts at 56° , separates from ethyl alcohol in small, prismatic rods, and is odourless.

Density Determinations.

The following density determinations were carried out in a pycnometer holding 4 c.c., and are compared with water at 4° :

l-Ethyl-n-propylcarbinol: at 13.5° , 0.8246; at 53.5° , 0.7946; at 84° , 0.7627; at 104° , 0.7428.

d-Ethyl-n-butylcarbinol: at 13° , 0.8248; at 50° , 0.7985; at 88° , 0.7603; at 127° , 0.7245.

d-Ethyl-n-amylcarbinol: at 19° , 0.8234; at 48° , 0.8016; at 89° , 0.7648; at 125° , 0.7302.

d-Ethyl-n-hexylcarbinol (as given in Part I), and at 124° , 0.7480.

l-Ethyl-n-heptylcarbinol: at 12.5° , 0.8310; at 48° , 0.8071; at 90° , 0.7715; at 134° , 0.7330.

l-Ethyl-n-octylcarbinol: at 17° , 0.8308; at 50° , 0.8076; at 81° , 0.7823; at 128° , 0.7426.

1-Ethyl-n-nonylcarbinol: at 32° , 0.8223; at 61° , 0.7999; at 91° , 0.7748; at 124° , 0.7467.

d-Ethyl-n-decylcarbinol: at 46° , 0.8139; at 69° , 0.7965; at 93° , 0.7755; at 128° , 0.7466.

1-Ethyl-n-decylcarbinol: at 43° , 0.8180; at 80° , 0.7889.

1-Ethyl-n-undecylcarbinol: at 53° , 0.8098; at 78° , 0.7896; at 98° , 0.7748; at 146.5° , 0.7354.

1-Ethyl-n-dodecylcarbinol: at 55° , 0.8115; at 82° , 0.7908; at 94° , 0.7816; at 132° , 0.7518.

1-Ethyl-n-tridecylcarbinol: at 67° , 0.8000; at 90° , 0.7843; at 119° , 0.7611; at 153° , 0.7335.

1-Ethyl-n-pentadecylcarbinol: at 73° , 0.8011; at 90° , 0.7876; at 121° , 0.7618.

Determination of the Rotatory Powers of the Carbinols in the Homogeneous State.

The determinations of the rotatory powers of the carbinols in the homogeneous state have been made in jacketed tubes, 50 mm. and 100 mm. in length, round which a heated mineral oil was circulated by a pump. The temperature was carefully observed by a standardised thermometer placed in the liquid under observation, and the general practice was to make a series of readings with (say) the yellow sodium light whilst the temperature was rising, and another series with the green mercury light whilst it was falling. In each case similar curves were obtained for both wave-lengths, and no evidence was obtained that any racemisation had ensued during the heating. The figures given below are either those obtained from observations in a 100 mm. tube or have been calculated for that length:

*1-Ethylpropylcarbinol: α_D at 22.5° , -1.62° ; at 58° , -1.64° ; at 87° , -1.68° ; and at 108° , -1.72° .

α_{gr} at 22.5° , -1.84° ; at 73° , -1.90° ; at 102° , -1.94° ; and at 117° , -1.96° .

d-Ethyl-n-butylcarbinol: α_D at 20.5° , $+6.68^{\circ}$; at 54° , $+6.54^{\circ}$; at 57° , $+6.52^{\circ}$; at 70° , $+6.46^{\circ}$; at 104° , $+6.34^{\circ}$; and at 130° , $+6.21^{\circ}$.

α_{gr} at 20.5° , $+7.88^{\circ}$; at 77° , $+7.54^{\circ}$; at 97° , $+7.46^{\circ}$; at 105° , 7.40° ; at 120° , $+7.34^{\circ}$; and at 134° , $+7.26^{\circ}$.

d-Ethyl-n-amylcarbinol: α_D at 18° , $+6.79^{\circ}$; at 23° , $+6.76^{\circ}$; at 55° , $+6.69^{\circ}$; at 63° , $+6.60^{\circ}$; at 94° , $+6.46^{\circ}$; at 114° , $+6.38^{\circ}$; at 130° , $+6.28^{\circ}$; and at 160° , $+6.05^{\circ}$.

α_{gr} at 23° , $+7.94^{\circ}$; at 42° , $+7.86^{\circ}$; at 52° , $+7.80^{\circ}$; at 63° ,

* *Methylethylcarbinol* (see p. 1941).

+7.76°; at 82°, +7.66°; at 93°, +7.62°; at 108°, +7.48°; at 120°, +7.36°; at 133°, +7.30°; and at 145°, +7.20°.

l-Ethyl-*n*-hexylcarbinol: α_D at 19°, -6.10°; at 48°, -6.12°; at 56°, -6.14°; at 62°, -6.12°; at 70°, -6.10°; at 87°, -6.00°; at 111°, -5.86°; at 128°, -5.74°; and at 152°, -5.52°.

α_{gr} at 19°, -7.12°; at 45°, -7.16°; at 52°, -7.14°; at 64°, -7.06°; at 80°, -7.00°; at 101°, -6.90°; at 112°, -6.84°; at 131°, -6.66°; and at 149°, -6.50°.

l-Ethyl-*n*-heptylcarbinol: α_D at 21°, -5.54°; at 47°, -5.42°; at 72°, -5.33°; at 92°, -5.19°; at 100°, -5.14°; at 132°, -4.90°; and at 148°, -4.78°.

α_{gr} at 19.5°, -6.42°; at 63°, -6.20°; at 68°, -6.16°; at 73°, -6.12°; at 91°, -6.100°; at 96°, -5.96°; at 112°, -5.86°; at 135°, -5.64°; and at 142.5°, -5.60°.

l-Ethyl-*n*-octylcarbinol: α_D at 22°, -5.21°; at 38°, -5.17°; at 58°, -5.12°; at 86°, -4.98°; at 100°, -4.90°; at 132°, -4.72°; and at 145°, -4.64°.

α_{gr} at 20.5°, -6.02°; at 43°, -5.96°; at 76°, -5.80°; at 95°, -5.70°; at 116°, -5.56°; at 128°, -5.54°; and at 157°, -5.28°.

l-Ethyl-*n*-nonylcarbinol: α_D at 29.5°, -4.80°; at 31°, -4.76°; at 36°, -4.68°; at 62°, -4.44°; at 70°, -4.38°; at 85°, -4.32°; at 100°, -4.24°; at 122°, -4.12°; at 135°, -4.10°; and at 157°, -4.06°.

α_{gr} at 30°, -5.54°; at 51.5°, -5.20°; at 76°, -5.00°; at 90°, -4.90°; at 112°, -4.80°; at 137°, -4.68°; and at 152°, -4.64°.

d-Ethyl-*n*-decylcarbinol: α_D at 42°, +5.04°; at 63°, +4.90°; at 92°, +4.72°; at 107°, +4.64°; at 120°, +4.56°; at 131°, +4.50°; and at 158°, +4.38°.

α_{gr} at 38°, +5.90°; at 68°, +5.66°; at 83°, +5.54°; at 102°, +5.40°; at 127°, +5.20°; at 150°+5.08°; and at 168°, +5.02°.

l-Ethyl-*n*-decylcarbinol: α_D at 76°, -4.82°.

l-Ethyl-*n*-undecylcarbinol: α_D at 42°, -4.74°; at 53°, -4.64°; at 79°, -4.52°; at 85°, -4.46°; at 105°, -4.40°; at 117°, -4.34°; at 138°, -4.18°; and at 166°, -4.02°.

α_{gr} at 41°, -5.49°; at 47.5°, -5.46°; at 53°, -5.40°; at 70°, -5.29°; at 90°, -5.19°; at 113°, -5.08°; at 119°, -5.04°; at 133°, -4.94°; and at 144°, -4.87°.

l-Ethyl-*n*-dodecylcarbinol: α_D at 53°, -4.40°; at 64°, -4.32°; at 84°, -4.20°; at 104°, -4.12°; at 134°, -4.02°; and at 158°, -3.92°.

α_{gr} at 46°, -5.14°; at 68°, -4.96°; at 75°, -4.92°; at 86°, -4.86°; at 99°, -4.78°; at 116°, -4.72°; at 130°, -4.64°; at 140°, -4.62°; and at 155°, -4.60°.

1-*Ethyl-n-tridecylcarbinol*: α_D at 50° , -4.14° ; at 57° , -4.12° ; at 90° , -3.94° ; at 114° , -3.78° ; and at 148° , -3.58° .

α_{gr} at 58° , -4.78° ; at 78° , -4.66° ; at 98° , -4.50° ; at 125° , -4.30° ; and at 149° , -4.14° .

1-*Ethyl-n-pentadecylcarbinol*: α_D at 64° , -3.84° ; at 77° , -3.78° ; at 102° , -3.64° ; at 120° , -3.58° ; at 141° , -3.50° ; and at 154° , -3.40° .

α_{gr} at 61° , -4.44° ; at 67° , -4.42° ; at 71° , -4.40° ; at 96° , -4.30° ; at 113° , -4.20° ; at 118° , -4.16° ; at 136° , -4.10° ; and at 161° , -3.80° .

For the purpose of testing whether the optical rotatory dispersion $\text{Na}_{\text{yellow}}/\text{Hg}_{\text{green}}$ is constant over the available range of temperature, new preparations of methyl-*n*-butyl-, -*n*-hexyl-, and -*n*-nonyl-carbinols, as well as of *n*-propylisopropylcarbinol and isopropyl-*n*-hexylcarbinol have been examined. The following polarimetric observations agree well with those recorded in Parts I and II.

d-*Methyl-n-butylcarbinol*: α_D at 20° , $+9.08^\circ$; at 42° , $+8.60^\circ$; at 64° , $+8.19^\circ$; at 80° , $+8.00^\circ$; at 96° , $+7.83^\circ$; at 110° , -7.73° ; and at 119° , -7.62° .

α_{gr} at 21° , $+10.82^\circ$; at 43° , $+10.06^\circ$; at 56° , $+9.79^\circ$; at 70° , $+9.49^\circ$; at 80° , $+9.33^\circ$; at 95° , $+9.13^\circ$; at 105° , $+9.07^\circ$; and at 123° , $+8.95^\circ$.

The values of the optical dispersive power calculated from the smoothed curves from these figures are: at 20° , 0.844; at 40° , 0.848; at 60° , 0.848; at 80° , 0.851; at 100° , 0.851; and at 120° , 0.848, the mean value being 0.848. This alcohol has been prepared recently in larger quantities, but the authors have not been able to prepare material with $[\text{M}]_D$ at the boiling point so high as that (11.3°) given in Part I, the value $[\text{M}]_D^{bp}$ 10.9° being the highest obtained lately.

d-*Methyl-n-hexylcarbinol*: α_D at 20° , $+8.05^\circ$; at 48° , $+7.54^\circ$; at 54° , $+7.38^\circ$; at 70° , $+7.13^\circ$; at 104° , $+6.76^\circ$; at 110° , $+6.68^\circ$; and at 142° , $+6.35^\circ$.

α_{gr} at 19° , $+9.61^\circ$; at 48° , $+8.90^\circ$; at 62° , $+8.55^\circ$; at 74° , $+8.36^\circ$; at 95° , $+8.07^\circ$; at 120° , $+7.80^\circ$; and at 139.5° , $+7.63^\circ$.

The values of the dispersive power calculated from these observations are: at 20° , 0.845; at 40° , 0.845; at 60° , 0.847; at 80° , 0.845; at 100° , 0.845; at 120° , 0.844; and at 140° , 0.842, the average value being 0.845.

d-*Methyl-n-nonylcarbinol*: α_D at 142° , $+5.24^\circ$.

α_{gr} at 23° , $+7.85^\circ$; at 45° , $+7.28^\circ$; at 57° , $+7.01^\circ$; at 70° , $+6.78^\circ$; at 95° , $+6.56^\circ$; at 113° , $+6.45^\circ$; at 135° , $+6.23^\circ$; and at 151° , $+6.12^\circ$.

From these and previously recorded (Part I) observations, the calculated values of the optical dispersive power are: at 20°, 0·849; at 40°, 0·849; at 60°, 0·854; at 80°, 0·854; at 100°, 0·847; at 120°, 0·844; and at 140°, 0·845, the average value being 0·849.

d-Propyl-isopropylcarbinol: α_D at 19°, +17·66°; at 31°, +17·48°; at 45°, +17·18°; and at 98°, +15·54°.

α_{gr} at 19°, +20·94°; at 30°, +20·64°; at 40°, +20·40°; at 55°, +20·08°; at 65°, +19·74°; at 98°, +18·38°; at 111°, +17·88°; at 116·5°, +17·46°; and at 121°, +17·22°. These observations, with others previously recorded, give the following values of the optical rotatory dispersive power: at 20°, 0·844; at 40°, 0·844; at 60°, 0·842; at 80°, 0·840; at 100°, 0·843; at 120°, 0·843; and at 140°, 0·842, the average value being 0·843.

isoPropyl-d-hexylcarbinol: α_D at 18·5°, +17·86°.

α_{gr} at 18·5°, +21·24°; at 40°, +20·60°; at 62°, +19·94°; at 98°, +18·46°; at 112°, +17·96°; at 127°, +17·42°; and at 147°, +16·50°. The values of the optical rotatory dispersive power calculated from these and previously recorded observations are: at 20°, 0·841; at 40°, 0·842; at 60°, 0·840; at 80°, 0·839; at 100°, 0·840; at 120°, 0·840; at 140°, 0·840; and at 160°, 0·841, the average value being 0·840.

*Determinations of the Rotatory Power in Absolute Ethyl.
Alcohol.*

Carbinols, CH₃·CH(OH)·R.

	Weight taken in grams.	Observed rotation.		
		α_D .	$[\alpha]_D$.	$[M]_D$.
Methyl-ethylcarbinol	1·0167	+1·48°	+14·55°	+10·77°
Methyl- <i>n</i> -propylcarbinol	1·0641	1·65	15·51	13·60
Methyl- <i>n</i> -butylcarbinol	1·0471	1·33	12·70	12·95
Methyl- <i>n</i> -amylcarbinol	1·0392	1·19	11·45	13·28
Methyl- <i>n</i> -hexylcarbinol	1·0923	1·07	9·79	12·73
Methyl- <i>n</i> -heptylcarbinol	1·1427	1·04	9·10	13·10
Methyl- <i>n</i> -octylcarbinol	1·0126	0·90	8·89	14·04
Methyl- <i>n</i> -nonylcarbinol	1·0229	0·83	8·11	13·95
Methyl- <i>n</i> -decylcarbinol	0·8694	0·69	7·94	14·76
Methyl- <i>n</i> -undecylcarbinol	1·0174	0·75	7·37	14·74

Carbinols, CH(CH₃)₂·CH(OH)·R.

<i>iso</i> Propylmethylcarbinol	0·9555	+0·51°	+5·34°	+4·70°
<i>iso</i> Propylethylcarbinol	1·0670	1·75	16·40	16·73
<i>iso</i> Propyl- <i>n</i> -propylcarbinol	0·9942	2·32	23·34	27·07
<i>iso</i> Propyl- <i>n</i> -butylcarbinol	1·0589	2·93	27·67	35·97
<i>iso</i> Propyl- <i>n</i> -amylcarbinol	0·9713	2·58	26·56	38·24
<i>iso</i> Propyl- <i>n</i> -hexylcarbinol	1·1242	2·73	24·28	38·36
<i>iso</i> Propyl- <i>n</i> -octylcarbinol	1·0002	2·15	21·50	39·99
<i>iso</i> Propyl- <i>n</i> -decylcarbinol	1·1852	2·18	18·34	39·38

Determinations of the Rotatory Power in Absolute Ethyl Alcohol (continued).

Carbinols, $C_2H_5 \cdot CH(OH) \cdot R$.

	Weight taken in grams.	Observed rotation. α_D .	$[\alpha]_D$.	$[M]_D$.
Ethyl- <i>n</i> -propylcarbinol	1.0426	-0.12°	1.15°	1.17°
Ethyl- <i>n</i> -butylcarbinol	1.0070	+0.97	9.63	11.17
Ethyl- <i>n</i> -amylcarbinol	0.9791	+1.09	11.13	14.47
Ethyl- <i>n</i> -hexylcarbinol	1.0182	+0.98	9.63	13.86
Ethyl- <i>n</i> -heptylcarbinol	0.9990	-0.62	6.21	9.81
Ethyl- <i>n</i> -octylcarbinol 1 ...	1.0449	-0.65	6.22	10.69
Ethyl- <i>n</i> -nonylcarbinol	1.1144	-0.68	6.10	11.35
Ethyl- <i>n</i> -decylcarbinol	0.9510	-0.64	6.73	13.46
Ethyl- <i>n</i> -undecylcarbinol	1.0728	-0.67	6.25	13.38
Ethyl- <i>n</i> -dodecylcarbinol	1.0988	-0.60	5.46	12.44
Ethyl- <i>n</i> -tridecylcarbinol	1.0461	-0.55	5.27	12.75
Ethyl- <i>n</i> -pentadecylcarbinol ...	1.0047	-0.48	4.78	12.91

Determination of Rotatory Power of Carbinols, $C_2H_5 \cdot CH(OH) \cdot R$, in Benzene.

Dextrorotatory Carbinols, $CH_3 \cdot CH(OH) \cdot R$.

Methyl- <i>n</i> -propylcarbinol ...	0.8059	+1.44°	+17.87°	+15.73°
Methyl- <i>n</i> -butylcarbinol	1.0111	1.41	13.95	14.23
Methyl- <i>n</i> -amylcarbinol	0.9918	1.36	13.71	15.90
Methyl- <i>n</i> -hexylcarbinol	1.1011	1.37	12.44	16.77
Methyl- <i>n</i> -heptylcarbinol ...	1.0090	1.19	11.90	16.98
Methyl- <i>n</i> -octylcarbinol	0.9953	1.14	11.46	18.10
Methyl- <i>n</i> -nonylcarbinol ...	1.0303	1.06	10.29	17.69
Methyl- <i>n</i> -decylcarbinol	0.6808	0.68	9.99	18.57
Methyl- <i>n</i> -undecylcarbinol ...	1.0180	0.89	8.74	17.48

	Weight taken in grams.	Observed rotation α_D .	$[\alpha]_D$.	$[M]_D$.	Observed rotation α_{gr} .	$[\alpha]_{gr}$.	$[M]_{gr}$.
<i>d</i> -Ethyl-methyl- carbinol	1.0632	+1.50	+14.11°	+10.44°	+1.71°	+16.09°	+11.91
<i>l</i> -Ethyl- <i>n</i> -pro- pylcarbinol ...	1.0356	-0.19	-1.83	-1.87	-0.28	-2.70	-2.75
<i>d</i> -Ethyl- <i>n</i> -bu- tylcarbinol ...	1.0092	+0.94	+9.31	+10.80	+1.08	+10.70	+12.41
<i>d</i> -Ethyl- <i>n</i> -amyl- carbinol	1.0196	+1.04	+10.20	+13.26	+1.16	+11.38	+14.79
<i>d</i> -Ethyl- <i>n</i> -hexyl carbinol	1.0417	+1.00	+9.60	+13.82	+1.13	+10.85	+15.62
<i>l</i> -Ethyl- <i>n</i> -hep- tylcarbinol ...	1.0434	-0.80	-7.67	-12.11	-0.94	-9.01	-14.24
<i>l</i> -Ethyl- <i>n</i> -octyl carbinol	0.9886	-0.70	-7.08	-12.18	-0.86	-8.70	-14.96
<i>l</i> -Ethyl- <i>n</i> -no- nylcarbinol ...	1.0737	-0.72	-6.71	-12.48	-0.89	-8.29	-15.41
<i>l</i> -Ethyl- <i>n</i> -decyl carbinol	0.9581	-0.70	-7.31	-14.62	-0.80	-8.35	-16.70
<i>l</i> -Ethyl- <i>n</i> -un- decylcarbinol.	1.0282	-0.75	-7.29	-15.60	-0.88	-8.56	-18.32
<i>l</i> -Ethyl- <i>n</i> -do- decylcarbinol.	0.9522	-0.64	-6.72	-15.32	-0.76	-7.98	-18.20
<i>l</i> -Ethyl- <i>n</i> -tri- decylcarbinol.	1.0650	-0.68	-6.38	-15.44	-0.83	-7.79	-18.85
<i>l</i> -Ethyl- <i>n</i> -penta- decylcarbinol.	1.0067	-0.62	-6.16	-16.63	-0.75	-7.45	-20.12

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MUNICIPAL TECHNICAL SCHOOL,
BLACKBURN.

CCVIII.—*The Rate of Hydration of Acid Anhydrides: Acetic, Propionic, Butyric, and Benzoic.*

By BERNARD HOWELL WILSDON and NEVIL VINCENT SIDGWICK.

THE method adopted in this work is essentially that described by Rivett and Sidgwick (T., 1910, **97**, 732, 1677). The rate of formation of the acid is determined by measuring the increase of the electrical conductivity of a solution of the anhydride in water. For this purpose it was necessary to know the conductivities of the acids investigated, up to the concentration obtained from a saturated solution of the anhydride. The viscosities were also measured, and an allowance was made for this on the assumption that Stokes' law holds for ions in solution, and hence that the ionic mobilities are inversely proportional to the viscosity.

I.—*Conductivity, Density, and Viscosity.*

Two cells were used, one having large vertical electrodes covered with grey platinum, and the other smaller horizontal plates coated with platinum black. It was originally intended to have grey platinum in the second cell also, but with the smaller electrodes the "minimum" was found to be so bad in the stronger solutions as to introduce an error larger than any likely to result from adsorption by the platinum black. A Wheatstone-Kirchhoff roller bridge was used,* together with a Nernst induction coil.

* It does not seem to be generally recognised, although it is obvious enough when once it is pointed out, that in conductivity measurements under the ordinary conditions of experiment, the sensitiveness of a Wheatstone bridge is practically proportional to the resistance of the bridge wire. The change of sound in the telephone for a displacement of the sliding contact by, say, 0.1 mm. with a metre bridge, will be proportional to the fall of potential over 0.1 mm. of the wire, and therefore to the difference of potential between the ends of the bridge. The

The dilutions were made in the cell, which was first partly filled with conductivity water, and then a solution of the acid of known strength added from a weight pipette. In all cases several series of measurements were made with different original solutions. The water was obtained from a Hartley still, and its conductivity at 25° was from 0.8 to 1.5 gemmhos.

At the dilute end of the conductivity curve, the water correction becomes very considerable. The error may be avoided in measuring the velocity of hydration, if we use water of the same quality for the velocity experiments; but if we are to determine the value of the dissociation constant, it is necessary to know how the correction is to be applied. Our results indicate that fairly constant values of the Ostwald dissociation constant are obtained, even at dilutions where the correction is a large fraction of the total conductivity, when the conductivity of the water is added to that of the solution. At extreme dilution, however, the values thus obtained are too high. The theoretical justification for adding the correction is not easy to understand. If the conductivity of the water is mainly due to hydrogen ion, a negative correction would be required. If it is due either to sodium hydroxide from the glass, to ammonia, or to ammonium carbonate, some positive correction is necessary. A further positive correction is probably required at the higher dilutions, owing to adsorption by the plates. The method of simply adding the conductivity of the water seems, judging by the results, to give approximately the correction required.

The densities of the solutions were determined with pyknometers of test-tube glass, of about 25 c.c. capacity, and the viscosities with Ostwald viscometers, the water values of which were four to five minutes.

In the following tables * are given (1) the volume normality, (2) the specific conductivity uncorrected for water, (3) the molecular conductivity μ , and (4) the dissociation constant K , corrected by adding the conductivity of the water, and further by multiplying by the viscosity.

resistance of the bridge wire, however, is small in comparison with that of the whole circuit—including the secondary coil of the inductorium—of which it forms a part. Hence the fall of potential between the ends of the bridge, and therefore its sensitiveness, vary very nearly with the resistance of the bridge wire.

* In Tables I—V only a portion of those measurements which were used in obtaining a mean value of K are quoted.

1.—Acetic Acid.

Kahlbaum's purest acid, which had been frozen out and drained off from the liquid, was used. μ_a was taken as 353.0.

TABLE I.

*Conductivity of Acetic Acid at 18°.**

Vol. norm.	Sp. cond.	Mol. cond.	$K \times 10^7$.
0.002807	0.07597	27.13	179.6
0.004462	0.09590	21.78	181.0
0.007703	0.12700	16.66	179.0
0.02246	0.2187	9.813	178.5
0.03470	0.2722	7.902	177.8
0.07273	0.3910	5.435	175.2
0.1702	0.5990	3.595	177.8
0.4480	0.9462	2.224	178.9
0.8118	1.211	1.639	175.9
1.599	1.504	—	—
2.939	1.638	—	—
4.143	1.576	—	—

* The values for acetic acid at 25° are given by Rivett and Sidgwick, *loc. cit.*, pp. 734—736.

*Viscosity and Density.**

Vol. norm.	Density.	Viscosity.
5.6658	1.0428	1.7042
1.9801	1.0163	1.2366

* Throughout this paper the densities and viscosities are referred to water at the same temperature as unity.

Three series of measurements were made. In the first and second, the conductivity of the water was 1.04 gemmhos; in the third, 1.23 gemmhos.

The mean of 16 values of K , from 182.0 to 175.2, is 178.8. The maximum divergence from the mean is 2.0 per cent. It will be seen from the table that the greatest differences occur at the beginning of each series, where any error arising from differences in adsorption at the electrodes of the two cells used will have the maximum effect.

By using this value for the dissociation constant of acetic acid, together with that (re-calculated) obtained by Rivett and Sidgwick, we can calculate the heat of ionisation Q for the temperature interval 18—25°:

$$K_{25} = 187.9$$

$$K_{18} = 178.8$$

$$\log_e \frac{187.9}{178.8} = - \frac{Q}{R} \left(\frac{1}{291} - \frac{1}{298} \right),$$

$$Q = -1.3421 \text{ kg. Cal.}$$

Lundén gives for temperatures from 10° upwards the value $-0.675 + 0.0315$ kg. Cal., but there is such divergence between the values of different observers, obtained by different methods, that it is impossible to judge of the correctness of this result.

2.—Propionic Acid.

Kahlbaum's purest acid was distilled twice, and the fraction boiling at 140.9 — 141.0° (uncorr.) was used; μ_{∞} was taken as 401.6 at 25° , and 349.0 at 18° .

TABLE II.

Conductivity of Propionic Acid at 25° .

Vol. norm.	Sp. cond.	Mol. cond.	$K \times 10^7$.
0.006776	0.1120	16.56	122.1
0.01445	0.1646	11.43	121.6
0.02581	0.2217	8.634	123.3
0.04862	0.3031	6.297	122.2
0.08097	0.3906	4.901	122.7
0.1469	0.5221	3.659	123.5
0.3649	0.7877	2.309	121.7
0.8990	1.087	—	112.4]
1.073	1.131	—	107.5]

In one of the two series, conductivity of water was 0.73 gemmhos; in the other, 1.20 gemmhos.

Viscosity and Density at 25° .

Vol. norm.	Density.	Viscosity.
1.817	(1.0107)	1.3542
1.370	1.0081	1.2668
0.9893	(1.0059)	1.1877
0.6496	(1.0039)	1.1244
0.4457	1.0026	1.0862
0.2594	1.0023	1.0500

Values in brackets were interpolated from the curve.

The values of K are not given below 0.36 normal, as at this point they begin to fall regularly. The mean of 21 values, ranging from 121.4 to 123.5 , gives K as 122.5 , with a maximum error of 0.9 per cent.

TABLE III.

Conductivity of Propionic Acid at 18°.

Vol. norm.	Sp. cond.	Mol. cond.	$K \times 10^7$.
0.001164	0.04094	35.17	135.7
0.003167	0.06884	21.75	134.4
0.006223	0.09819	15.79	135.2
0.01784	0.1674	9.416	134.8
0.02613	0.2056	7.917	137.6
0.03500	0.2347	6.751	134.5
0.04510	0.2695	6.032	137.1
0.05936	0.3085	5.259	136.9
0.09609	0.3866	4.099	134.7
0.1715	0.5094	3.069	134.2
0.3215	0.6794	—	134.0]
0.6564	0.9858	—	127.6]
0.9284	0.9942	—	122.0]

In the first two of the three series, conductivity of water was 0.70 gemmhos; in the third, 1.00 gemmhos.

The molecular conductivity at infinite dilution was taken as 349.0.

The mean of 31 values of K , ranging from 137.8 to 134.2, is 134.8, with a maximum error of 1.5 per cent.

Viscosity and Density at 18°.

Vol. norm.	Density.	Viscosity.
1.817	(1.0107)	1.3861
1.370	1.0081	1.2786
0.9825	1.0059	1.1958
0.6496	1.0039	1.1241
0.4457	1.0031	1.0852
0.2594	1.0018	1.0503

Taking the values $K_{25} \times 10^7 = 122.5$, and $K_{18} \times 10^7 = 135.8$, we get the heat of ionisation, $Q = +2.529$ kg. Cal. Arrhenius gives $Q = +0.183$ kg. Cal.

3.—*Butyric Acid (normal).*

Kahlbaum's purest acid was redistilled, and the fraction boiling at 163—163.5° (uncorr.) was used; μ_a was taken as 397.7 at 25°, the only temperature at which experiments were made.

TABLE IV.

Conductivity of Butyric Acid at 25°.

Vol. norm.	Sp. cond.	Mol. cond.	$K \times 10^7$.
0.001026	0.04372	42.61	139.1
0.001875	0.06047	32.25	139.3
0.003415	0.08290	24.28	139.5
0.005002	0.1012	20.23	139.7
0.007417	0.1229	16.71	139.4
0.01411	0.1718	12.17	139.8
0.02467	0.2271	9.203	138.8
0.04987	0.3240	6.497	140.0
0.1003	0.4547	4.645	139.4
0.19158	0.6122	—	137.6]
0.2328	0.6650	—	136.0]

Two series: conductivity of water 1.56 and 1.20 gemmhos respectively.

Viscosity and Density.

Vol. norm.	Density.*	Viscosity.
0.4771	1.00176	1.1231
0.2696	1.00100	1.0675
0.06240	1.00024	1.0156

* The values for the density are taken from Lüdeking (*Jahresber.*, 1886, 216).

Mean of 17 values of K , from 141.3 to 138.8, is 139.7. Maximum error, 1.0 per cent.

II.—Rate of Hydration of Anhydrides.

These measurements were carried out in the cells previously used for the conductivities. With the liquid anhydrides, a measured volume was added to the required volume of water, already warmed in the thermostat, and then the whole shaken violently for a short time, and poured into the cell. The benzoic anhydride, being solid, was finely powdered, shaken with water, and the liquid was sucked through a glass-wool filter into the cell.

The conductivity of the solution was measured from time to time, and the amount of acid present determined by interpolation on the conductivity curves. As before, the results were corrected for viscosity, on the assumptions (a) that the ionic velocity is inversely proportional to the viscosity, and (b) that the viscosity of a solution of an anhydride is equal to that of an equivalent solution of the corresponding acid. The latter has been shown to be approximately true for acetic anhydride.

The results are calculated on the unimolecular formula.

1.—Acetic Anhydride.

The material was Kahlbaum's anhydride "free from homologous anhydrides."

In the following table, the first column gives the (volume) normality of the acid at the end of the experiment; the second, the initial equivalent normality of the anhydride at the time, which was taken as =0 for calculating the velocity. The values of K are in each case the mean of more than twenty observations. The expression K' in the last column is explained below.

TABLE VI.

Hydration of Acetic Anhydride at 18°.

Final norm. of acid.	Initial norm. of anhydride.	K .	$K' = K \times \eta^2/C_w$.
0.00648	0.00543	0.000762	0.000763
0.00978	0.00821	742	744
0.03336	0.02655	759	765
0.05152	0.04064	737	746
0.1054	0.08513	716	735
0.1743	0.1231	739	772
0.1856	0.1490	745	784
0.1959	0.1452	741	783
0.2602	0.2096	723	779
0.2840	0.2155	729	789
0.2948	0.2436	735	800
0.3509	0.2913	718	794
0.6778	0.4875	663	806
0.7109	0.5262	649	794
1.2011	1.0349	591	823
2.2050	1.9710	459	828

For the sake of comparison, the results obtained by Rivett and Sidgwick at 25° are given in table VII, with the corresponding corrections. The first column gives the normality, the second the observed velocity constant K , and the third the corrected $K' = K \times \eta^2/C_w$.

TABLE VII.*

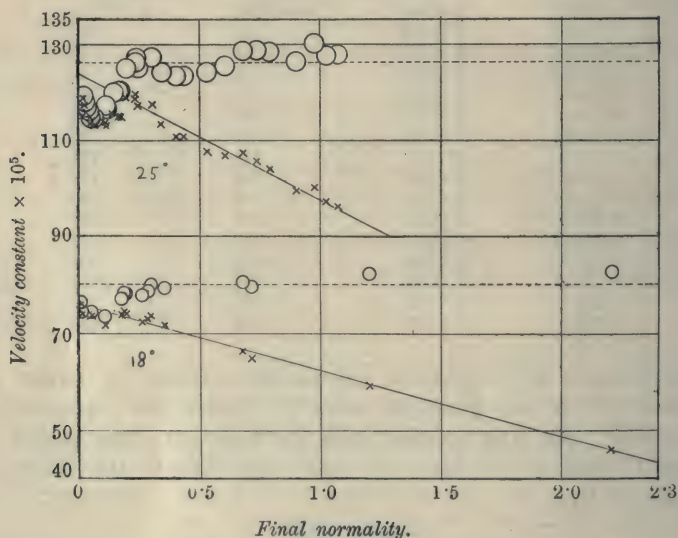
Hydration of Acetic Anhydride at 25°.

Normality.	K .	$K' = K \times \eta^2/C_w$.	Normality.	K .	$K' = K \times \eta^2/C_w$.
0.02015	0.001186	0.001192	0.4010	0.001105	0.001233
0.03307	1157	1168	0.4355	1103	1233
0.04883	1133	1146	0.5300	1075	1240
0.07575	1137	1158	0.6040	1067	1253
0.1160	1131	1164	0.6785	1072	1284
0.1670	1148	1202	0.7345	1056	1285
0.1949	1186	1249	0.7895	1039	1281
0.2339	1184	1261	0.8995	994	1261
0.2348	1192	1270	0.9745	1002	1298
0.2449	1169	1249	1.0255	971	1274
0.3028	1173	1271	1.0705	961	1276
0.3425	1130	1240			

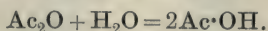
* Some of the earlier values are omitted in this table, but they are given in the diagram.

The results are plotted in the diagram against the final concentration of the acid; and for comparison, those obtained at 25° (R. and S.) are added. The crosses indicate the observed values ($K \times 10^5$); the circles, the values corrected as described below ($K \times \eta^2/C_w \times 10^5$); the radius of the circle corresponds to an error of 1.5 per cent. They show two peculiar phenomena: first, an irregularity at the dilute end, consisting of a fall as the concentration increases from its lowest value to about $N/10$, followed by a rise from $N/10$ to about $N/5$; and secondly, a steady fall with increase of concentration from $N/5$ upwards.

The second phenomenon may be considered first. This has the



same value—about 23 per cent. for an increase from $N/5$ to $1.2N$ —at 18° and 25°. It is confirmed by the work of Orton and Jones (T., 1912, 101, 1709), who measured the velocity of this reaction by a wholly different method, and with a much greater concentration of acid. One influence which would cause a fall in the velocity constant is the fall in the concentration of the water as the amount of acid increases. This, however, can be allowed for. The real reaction is, of course, bimolecular:



It can only be treated as unimolecular if the concentration of the water is taken as constant, which is not strictly the case, except at extreme dilution. We can, however, assume that this remains sensibly constant during an experiment; that is, that the change

in concentration due to the water taken up in the reaction is negligible, since this does not exceed 2 per cent., even when the initial (equivalent) concentration of the anhydride is normal. We are therefore justified in calculating on the unimolecular formula, but the values obtained must be divided by the concentration of the water in each experiment (that in pure water being taken as unity) to give the true velocity constant.

This correction, however, is far from sufficient to account for the observed fall; in fact, it only amounts to about 6 per cent. for an increase of $1N$, whilst the fall is some four times as great. Another factor which may explain the fall is the increase in the viscosity of the medium. If we suppose that the mobilities of the two reacting molecular species are inversely proportional to the viscosity, then the observed values ought to be multiplied by the square of the viscosity, in order to give the intrinsic velocity constant.

This conclusion may be expressed as follows: If the rate of reaction is proportional to the product of the concentrations of the two reacting substances, divided by the viscosity of the solution, we have:

$$\frac{dx}{dt} = K' \times \frac{C_{anh.}}{\eta} \times \frac{C_w}{\eta}.$$

Assuming that C_w and η remain constant during an experiment, this gives on integration:

$$\frac{1}{t} \log \frac{A}{A-x} = \frac{K' \times C_w}{\eta^2},$$

where A is the initial concentration of the anhydride, and x its concentration at time t .

The figures given in the last column of the table represent the values of the observed velocity constants corrected in this way for the concentration of the water, and for the viscosity of the medium.

It will be seen that the values of K' (from about 0.18 normal upwards) show a fair approximation to constancy, especially considering that the correction in the strongest solution is upwards of 80 per cent. The mean of all the results above 0.2 normal is 0.001263 at 25° and 0.0008017 at 18°; these are represented by the dotted horizontal lines on the diagram, and are in both cases a little higher than the values for infinite dilution obtained by drawing a straight line through the values of K for the stronger solutions and extrapolating to zero normality; but we may take this mean value as representing the specific velocity constant of this anhydride for the purpose of comparison with other anhydrides. The temperature-coefficient $K_{25} \div K_{18}$ is 1.575 for 7°,

and hence for 10° , 1.914. The "half-life" period for acetic anhydride is $3' 58''$ at 25° and $6' 15''$ at 18° .

The irregularity at the dilute end of the curves is clearly real, and not due to experimental error. It was observed in both sets of experiments—at 18° and 25° —with different samples of acid and anhydride, in different cells, and with a different conductivity curve in each case; also, as will be seen later, there are indications of the same phenomenon with other anhydrides. It is, however, not easy to see how it is to be explained. A natural suggestion is that it is due to catalytic agents. Now our results indicate clearly that the catalytic influence of hydrogen ion on the hydration of these anhydrides in water is negligible. In our various experiments the concentration of hydrogen ion was varied in the ratio of 8 or 9 to 1, and, as we have shown, the increase was accompanied by an actual fall in the velocity constant. In the same way, Orton and Jones (*loc. cit.*) find that the effect of strong acids is very small in aqueous solution; its greater value in non-aqueous solvents is presumably due to the undissociated acid molecules. On the other hand, hydroxyl ion has a very great catalytic power, as was shown by Orton and Jones, who argue (*loc. cit.*, p. 1715) that our conclusion that the mechanism of hydrolysis of anhydrides must be different from that of esters and amides, is incorrect. The fact, however, still remains that whilst the latter reactions proceed in aqueous solution at a rate proportional to the concentration of hydrogen ion, the former are very nearly, if not quite, independent of this. The influence of hydroxyl ion, on the other hand, seems to be much the same in both series of reactions, although it has not been found possible to measure its effect with any accuracy in the case of anhydrides.* Since in aqueous solution the product of the concentrations of hydrogen and hydroxyl ions is constant, it is obviously not enough to assume that the rate of hydration is proportional to the concentration of hydroxyl ion, and independent of the hydrogen. If this were all, the rate would fall continuously in proportion to the rise of hydrogen ion, owing to the corresponding fall in the hydroxyl ion. The expression for the catalytic influence must be of such a form that the velocity increases when C_{OH} rises above 10^{-7} , but does not fall, or only slightly, when C_{OH} falls below that value, that is, when the solution becomes acid. These conditions are fulfilled by an equation of the form:

$$K' = \alpha + \beta \cdot C_{OH}.$$

If we suppose that α and β are of the same order of magnitude,

* In a subsequent paper it will be shown that the rate of hydration of camphoric anhydride is increased by the presence of hydroxyl ions, and roughly in proportion to the concentration of the latter.

it is obvious that when C_{OH} is high, the first will be negligible in comparison with the second, and hence the velocity will be practically proportional to the concentration of hydroxyl ion (hydroxyl catalysis of the ordinary kind). Where C_{OH} falls below a certain value, the second term will become negligible, and the velocity will not be affected by any further fall in C_{OH} . This is what appears to happen with acetic anhydride. In alkaline solution (that is, when $C_{OH} > 10^{-7}$) the velocity is proportional (more or less) to the hydroxyl ion; but in acid solution ($C_{OH} < 10^{-7}$) it is independent of it. This view also affords a partial explanation of the irregularity observed at the dilute end of the curve. The rapid fall observed up to a concentration of about $N/10$ may possibly be due to the diminution in hydroxyl ions. The rise between $N/10$ and $N/5$ we do not profess to explain.

2.—Propionic Anhydride.

Kahlbaum's purest anhydride was used. It was twice distilled, and the fraction boiling at 167—169° was employed.

TABLE VIII.

Hydration of Propionic Anhydride at 25°.

Final norm. of acid.	Initial norm. of anhydride.	K .	$K' =$ $K \times \eta^2 / C_{w_0}$
0·00830	0·006013	0·000581	0·000583]
0·02448	0·02122	600	607]
0·06145	0·05163	605	621
0·07852	0·05974	598	617
0·1097	0·08722	586	614
0·1232	0·1010	594	628
0·1510	0·1156	579	619
0·2688	0·2300	580	619
Mean.....			0·000620

TABLE IX.

Hydration of Propionic Anhydride at 18°.

Final norm. of acid.	Initial norm. of anhydride.	K .	$K' =$ $K \times \eta^2 / C_{w_0}$
0·002668	0·002301	0·000407	0·000407]
0·003073	0·002578	409	409]
0·01090	0·009227	403	405]
0·01662	0·01405	413	415
0·04342	0·03827	412	418
0·06040	0·05115	407	417
0·07250	0·06482	396	408
0·2027	0·1717	383	419
0·1941	0·1756	389	423
0·1981	0·1759	393	429
0·2400	0·2082	383	425
Mean			0·000419

As before, the last column gives the values of the velocity constant, corrected for the concentration of the water and for the viscosity. These figures show a certain tendency to rise with increasing concentration; but the small range of concentrations examined (owing to the sparing solubility of this anhydride in water) make it difficult to draw any definite conclusions. For the purpose of comparison with other anhydrides, it is desirable to obtain a value for the velocity at infinite dilution, which should be the mean K' if the corrections are justified.

At 25° the mean K' (excluding the first two values) is 0.0006195; the maximum error is 1.4 per cent. At 18° the mean (excluding the first three) is 0.0004191, with a maximum error of 2.8 per cent. The ratio $K'_{25} \div K'_{18}$ is thus 1.48, and hence the temperature-coefficient for 10° is 1.75. The "half-life" period is 8' 6" at 25° and 11' 58" at 18°.

3.—Butyric Anhydride (Normal).

Kahlbaum's "puriss" anhydride was twice distilled, and the fraction boiling at 191—194° was used. The velocity was only measured at 25°.

TABLE X.

Hydration of Butyric Anhydride at 25°.

Final norm. of acid.	Initial norm. of anhydride.	K .
0.007457	0.006757	0.000338
0.01111	0.01032	343
0.01394	0.01225	334
0.03536	0.01654	345
Mean.....		0.000340

The slight solubility of the anhydride makes it impossible to extend the range of concentrations, and hence the correction is too small to be worth applying. The mean value of K is 0.000340, corresponding with a "half-life" period of 14' 46".

The maximum initial concentration of the anhydride obtained was about 0.017 equivalent-normal; this may be taken as approximately its solubility in water at 25°.

4.—Benzoic Anhydride.*

Kahlbaum's "puriss." was twice recrystallised from alcohol. The finely-ground solid was shaken with water at 25°, and the solution filtered into the cell through a plug of glass-wool.

* The measurements of the conductivity of benzoic acid required for these determinations are omitted. Owing to the very high dilutions, they have no absolute value, depending on the nature of the impurities in the water and the size and character of the electrodes.

TABLE XI.

Hydration of Benzoic Anhydride at 25°.

Final norm. of acid.	Initial norm. of anhydride.	K.
0·0000811	0·0000779	0·000158
669	597	163
557	532	160
832	445	152
442	400	155

Mean K 0·000158. "Half-life" period 31'45".

The anhydride is very sparingly soluble. The highest concentration obtained was below 0·00008 equivalent-normal, which may be taken as the solubility in water at 25°. This naturally leads to a large experimental error. The highest conductivity measured in any of the experiments with benzoic anhydride was less than 40 gemmhos.

5.—*Monochloroacetic Anhydride.*

In order to test the influence of negative substituents on the velocity, an attempt was made to measure the rate of hydration of this anhydride. It was prepared by Bischoff and Walden's method (*Ber.*, 1894, **27**, 2949), the acid being distilled in a vacuum with phosphoric oxide. The distillate solidifies to a crystalline mass, melting at 46°. The rate of hydration was found to be far too great for measurement at 18° or 25°. Some of the substance was placed on a glass-wool filter dipping into the cell, which stood in a bath of ice and water. Water cooled to 0° was rapidly drawn through the filter into the cell, which was shaken, and the conductivity measured at once. The first reading was taken within half a minute of the time when the water first came in contact with the anhydride; it is scarcely possible to shorten this period, as the cell must be shaken to make the solution homogeneous. Under these conditions there were indications of a subsequent rise of conductivity, but this did not amount to 5 per cent. If we assume, as an outside estimate, that 5 per cent. of the anhydride was still present after thirty seconds, the value of K would be 0·042 at 0°. At 25° the change must be at least five times as rapid, giving 0·2 as the velocity constant, and 1·5 seconds as the "half-life" period. It thus appears that the replacement of hydrogen by chlorine makes the velocity constant at least one hundred and fifty times as large. The same substitution increases the ionisation constant nearly ninety times,

Conclusion.

The various physical constants we have determined for these acids and their anhydrides are given in the following table. As regards the first two columns, the density and viscosity curves for the acids are so nearly straight that we may assume the increase of density and of viscosity (the values for water at the same temperature being in both cases taken as unity) to be proportional to the normality. These values are also found to be practically the same at 18° as at 25°. The values of the solubility of the anhydrides are only rough, being estimated from the greatest concentrations observed in each case. They are expressed in equivalent normalities.

It will be seen that the introduction of a CH₂ into the acyl group lowers the velocity to about a-half, and the introduction of a chlorine atom increases it more than one hundred and fifty times; whilst the replacement of the methyl in acetic anhydride by phenyl diminishes it to an eighth.

TABLE XII.

Acids.

	$(\Delta - 1)/n$.	$(\eta - 1)/n$.	$K_{25} \times 10^7$.	$K_{18} \times 10^7$.
Acetic	0.0082	0.112	187.9	178.8
Propionic.....	0.0060	0.193	122.5	135.8
Butyric	0.0037	0.253	139.7	—
Monochloroacetic ...	—	—	15500	—

Anhydrides.

	$K_{25} \times 10^3$.	$K_{18} \times 10^3$.	Temp.-coeff. for 10°.	Solubility.
Acetic	1.243	0.802	1.91	2 <i>N</i> at 18°
Propionic	0.620	0.419	1.75	0.2 <i>N</i> „ 18
Butyric.....	0.340	—	—	0.017 <i>N</i> „ 25
Monochloroacetic	200 ?	—	—	—
Benzoic	0.158	—	—	0.00008 <i>N</i> „ 25

Böeseken, Schweitzer, and van der Want have expressed the opinion (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 622) that a high dissociation constant necessarily implies a high rate of hydration. It is clear, however, that there is no necessary connexion between the two in those anhydrides (such as those which we have examined) where the hydration is not measurably reversible. The results obtained with monobasic acids confirm the conclusions arrived at from the study of the dibasic compounds (see T., 1910, **97**, 1684). The rate of hydration and the dissociation constant show a general tendency to rise and fall together, but

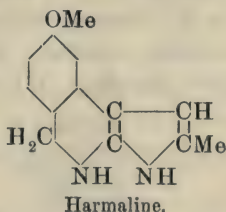
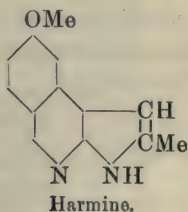
there are exceptions to this rule; and it is clear that whilst some factors tend to increase both, they are not the only factors concerned. A lengthening of the chain, which has little effect on the dissociation, diminishes the rate of hydration; the introduction of the heavy phenyl group, although it causes a marked increase in the ionisation, still further diminishes the reaction constant; but a chlorine atom, which enormously increases the dissociation constant with a comparatively small change in the structure and weight of the molecule, produces a correspondingly large rise in the rate of hydration.

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CCIX.—*Harmine and Harmaline. Part II. The Synthesis of isoHarman.*

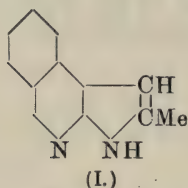
By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

IN Part I of this investigation of the constitution of harmine and harmaline (T., 1912, 101, 1775) we were able to show that these substances, in all probability, are derivatives of *isoquinoline*, and that their constitutions are probably represented by the formulæ:

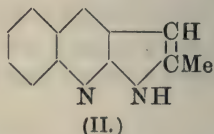


We, however, thought it desirable to obtain further evidence in support of the *isoquinoline* structure of these substances, and, in the present communication, we describe synthetical experiments undertaken with this object in view. O. Fischer (*Chem. Centr.*, 1901, i, 957) has shown that the methoxy-group in harmine may be eliminated by the following series of reactions. Harmine is converted by the action of hydrochloric acid at 140–170° into harmol, the methyl group being eliminated in the usual manner, and when harmol is heated with zinc chloride ammonia it yields aminoharman by the replacement of the hydroxy- by the amino-group. Lastly, the amino-group in aminoharman may be replaced

by hydrogen by the aid of the diazo-reaction, and the substance thus obtained has been named "*harman*." The problem in connexion with the constitution of harman is the same as that which we have mentioned in the case of harmine and harmaline; it is necessary to decide whether harman is a derivative of *isoquinoline* or of *quinoline*, that is to say, whether its structure is to be represented by (I) or by (II):



or



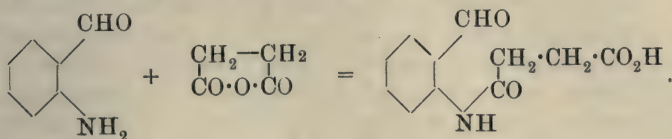
It is clear that, if this point is definitely decided in the case of harman, there can no longer be any doubt as to the *isoquinoline* or *quinoline* structure of harmine and harmaline. It seemed to us that this matter might best be decided by synthesising one of the substances just represented, and we selected the *quinoline* derivative (II) because it was thought that its synthesis would probably present less difficulty than that of the *isoquinoline* derivative (I).

Substance (II) is an indole derivative, in which the benzene ring is replaced by *quinoline*, and is therefore somewhat similarly constituted to 2-methylindole, and the most obvious process for its synthesis seemed to be the application of the Emil Fischer indole synthesis to *acetone-2-quinolylylhydrazone*, which should yield substance (II) according to the scheme:

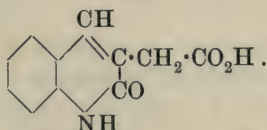


We therefore prepared *acetone-2-quinolylylhydrazone* by the condensation of acetone with 2-quinolylylhydrazine, but all attempts to convert it into the indole derivative by heating with hydrochloric acid, zinc chloride, or other condensing agents were unsuccessful, hydrolysis occurring in most of the experiments. As the only other method of attack seemed to be to build up the substance of formula II from a simpler starting point, we experimented in this direction, and ultimately accomplished the synthesis in the following manner. In the first place, *o-aldehydosuccinanilic acid*

(m. p. 115°) was prepared by condensing *o*-aminobenzaldehyde with succinic anhydride in boiling xylene solution:

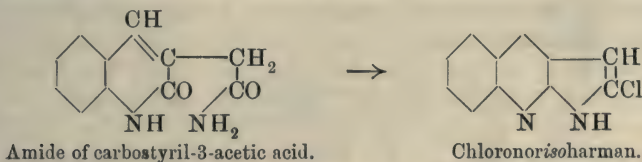


The aqueous solution of the sodium salt of this anilic acid was then digested with weak alkali, when internal condensation took place with the formation of *carbostyril-3-acetic acid* (m. p. 270°),

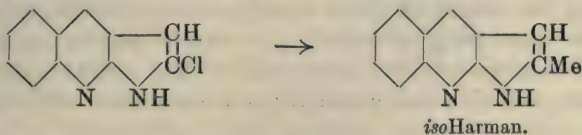


a condensation which closed the second ring of the formula.

The acid was then converted into the methyl ester (m. p. 175°), and this into the amide (m. p. 258°), which, when boiled with phosphoryl chloride, undergoes a remarkable reaction, which closes the third ring of the formula, and *chloronorisoharman* (m. p. 127°) is produced:

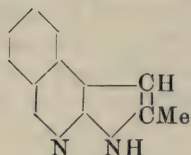


The last step in the synthesis of *isonorharman*, namely, the replacement of the chlorine atom in *chloronorisoharman* by the methyl group, proved to be a difficult operation (compare p. 1984),



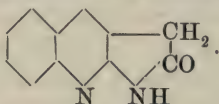
but it was ultimately accomplished by adding the chloro-derivative to a solution of magnesium methyl iodide in boiling *isoamyl* ether. *isoHarman* crystallises well from methyl alcohol, and melts at 213—215°, and although it has properties which are, as indeed might be expected, strikingly similar to those of *harman* (m. p. 230°), it is certainly not identical with that substance, and it follows, therefore, that *harman* cannot be this quinoline deriv-

ative, but must have the *isoquinoline* structure represented by the formula:

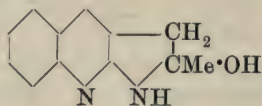


There can therefore be little doubt that the constitutional formulæ for harmine and harmaline suggested at the commencement of this communication do, in fact, actually represent these substances.

When chloronor*isoharman* is digested in acetic acid solution with dry potassium acetate it undergoes a curious decomposition, and is converted into a substance melting at 235°, which is evidently either hydroxynor*isoharman*, the lactim, or more probably the corresponding *lactam* of 2-aminoquinoline-3-acetic acid:

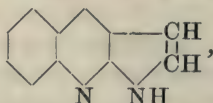


A series of experiments were made in the hope that this substance might react with magnesium methyl iodide to yield hydroxydihydro*isoharman*,



from which *isoharman* should result by the elimination of water, but the process did not take place under the conditions we employed.

During the course of these experiments it was thought that it would be interesting to reduce chloronor*isoharman*, and thus to obtain *norisoharman* or 12-quinindole,* the parent substance of *isoharman*, and this was found to be a much more difficult matter



than we had anticipated, since most of the usual reducing agents failed to produce the desired result, but ultimately we were able to bring about the reduction by using tin and hydrochloric acid

* For an explanation of the nomenclature of this substance, see T., 1912, 101, 1787.

at the ordinary temperature under the conditions described on p. 1983.

12-*Quinindole* appears to be the first representative of this class of substance; it melts at 85° , and is a strong base, which yields readily soluble and stable salts. It has little similarity to its 2-methyl derivative (*isoharman*), which melts at a much higher temperature (215°), is much less soluble in organic solvents, and yields salts which are also much less soluble than those of 12-quinindole.

It does not often happen that the mere substitution of hydrogen by methyl produces such a striking modification in the properties of the parent substance.

EXPERIMENTAL.

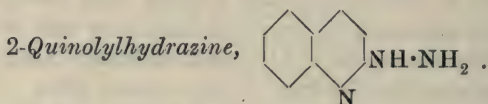
1-Methylquinolone, 2-Chloroquinoline, and 2-Quinolylhydrazine.

1-Methylquinolone has already been prepared from carbostyryl by methylation in methyl-alcoholic solution with methyl iodide in the presence of sodium hydroxide (Friedländer and Müller, *Ber.*, 1887, **20**, 2009), and by the oxidation of quinoline methiodide with potassium ferricyanide (Decker, *J. pr. Chem.*, 1893, [ii], **47**, 31; compare also Ostermayer, *Ber.*, 1885, **18**, 594, and Bernthsen and Hess, *ibid.*, 37); also by the action of potassium hydroxide on 2-iodoquinoline methiodide (Roser, *Annalen*, 1894, **282**, 377), but we have found that a more convenient method of preparation than any of these is the following. Methyl sulphate (50 grams) is gradually added to quinoline (50 grams), the vigorous reaction being controlled by cooling with water; the solid product is dissolved in water, mixed with a solution of freshly-recrystallised potassium ferricyanide (300 grams), and the whole made up to 2500 c.c. with water and transferred to a bottle. A considerable quantity of ether is poured in, and then potassium hydroxide (10 per cent.) added in small quantities at a time until the liquid is strongly alkaline, the whole being well shaken after each addition. The bottle is then shaken for ten minutes on the machine, the colourless ethereal solution separated, washed, dried over anhydrous potassium carbonate, and evaporated, when a solid residue of nearly pure 1-methylquinolone is obtained, the yield being 55 grams, or 90 per cent. of that theoretically possible.

The substance may be purified by recrystallisation from light petroleum, from which it separates in needles melting at 74° and having a pleasant aromatic odour.

2-Chloroquinoline.—The conversion of 1-methylquinolone into 2-chloroquinoline, a change which takes place with the elimination

of the methyl group, has been described by O. Fischer (*Ber.*, 1898, **31**, 612), who heated methylquinolone with a mixture of phosphorus pentachloride and phosphoryl chloride for eight hours at 130—140°, but we find that a higher temperature is necessary. 1-Methylquinolone (54 grams) is heated with phosphorus pentachloride (100 grams) and phosphoryl chloride (50 grams) for nine hours in an oil-bath kept at 175°. The hydrochloride of methylquinolone, which separates at first as a solid, soon liquefies, and the homogeneous liquid is distilled until the phosphoryl chloride has passed over and the excess of pentachloride commences to sublime; the residue is then carefully decomposed by water, excess of potassium hydroxide is added, and the whole distilled in steam. The distillate is extracted with ether, the ethereal solution dried over solid potassium hydroxide, evaporated, and the chloroquinoline distilled, when it passes over at 268°/744 mm., crystallises, and melts at 38°, the yield being 85—90 per cent. of that theoretically possible.



This substance was first prepared by Marckwald and Meyer (*Ber.*, 1900, **33**, 1885), who obtained it, together with 2-hydrazoquinoline, by heating 2-chloroquinoline with a large excess of hydrazine hydrate at 140° for six hours in sealed tubes. As we required considerable quantities of this substance, we endeavoured to improve this troublesome method of preparation, and find that 2-quinolylhydrazine is produced almost quantitatively when a mixture of 2-chloroquinoline (12 grams) and hydrazine hydrate (50 grams) is boiled in a flask with a ground-in condenser on the sand-bath for an hour. The orange-yellow liquid is distilled under diminished pressure until the excess of hydrazine hydrate has been recovered, the residue mixed with hot water, when the hydrazine soon separates in orange crystals, and after one crystallisation from benzene melts at 142—143°. The yield is 11 grams, and the substance is quite free from 2-hydrazoquinoline.

Acetone-2-quinolylhydrazone, $\text{C}_9\text{H}_6\text{N}\cdot\text{NH}\cdot\text{N}:\text{CMe}_2$.—In order to prepare this substance, 2-quinolylhydrazine is dissolved in excess of acetone, and, after remaining for five minutes, water is carefully added, and the whole well rubbed with a glass rod, but crystallisation is much facilitated by the addition of a crystal from a previous operation. The solid mass is collected and recrystallised from light petroleum (b. p. 50—60°), from which the substance

separates in stout, pale yellow, prismatic needles, which melt at 100° with slight previous softening:

0.1177 gave 0.3138 CO_2 and 0.0712 H_2O . $\text{C}=72.7$; $\text{H}=6.7$.

0.1171 „ 21.2 c.c. N_2 at 16° and 756 mm. $\text{N}=21.1$.

$\text{C}_{12}\text{H}_{13}\text{N}_3$ requires $\text{C}=72.4$; $\text{H}=6.5$; $\text{N}=21.1$ per cent.

Experiments made with the object of converting this substance into *isoharman* (compare p. 1974) by heating with zinc chloride according to Emil Fischer's method, were unsuccessful, since, although the conditions were greatly varied, the only product which could be isolated was the zinc chloride double salt of quinolyldiazine. Acid reagents, such as sulphuric acid or concentrated aqueous hydrochloric or hydrobromic acids, simply hydrolyse the substance to acetone and quinolyldiazine without any internal condensation taking place, but the cause of the failure is still being investigated.

o-Aldehydosuccinanilic Acid, $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$.

The best conditions for the preparation of this substance seem to be the following. Pure succinic anhydride (20 grams) is dissolved in carefully dried, boiling xylene (200 c.c.), the lamp removed, and then *o*-aminobenzaldehyde (24 grams)* added all at once. The liquid boils, and, on keeping, soon clouds, and deposits a nearly colourless, syrupy layer, which solidifies overnight, and crystals also separate in quantity from the xylene solution. The xylene is decanted, the crystals washed with benzene, and recrystallised from methyl ethyl ketone, from which the anilic acid separates in crusts of glistening prisms. The xylene solution, after concentration under diminished pressure, yields a further small quantity of the same substance, the total yield being about 80 per cent. of that theoretically possible:

0.1483 gave 0.3252 CO_2 and 0.0688 H_2O . $\text{C}=59.8$; $\text{H}=5.1$.

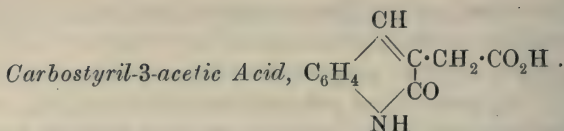
0.1334 „ 0.2927 CO_2 „ 0.0622 H_2O . $\text{C}=59.7$; $\text{H}=5.2$.

0.1429 „ 8.0 c.c. N_2 at 13° and 747 mm. $\text{N}=6.5$.

$\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}$ requires $\text{C}=59.7$; $\text{H}=5.0$; $\text{N}=6.3$ per cent.

o-Aldehydosuccinanilic acid melts at 114 – 115° , and dissolves readily in most organic solvents; it is sparingly soluble in cold, but dissolves somewhat in boiling water, and separates on cooling in long, glistening, colourless needles.

* For the preparation of *o*-aminobenzaldehyde, by the reduction of *o*-nitrobenzaldehyde with ferrous sulphate and ammonia, see Friedländer (*Ber.*, 1882, 15, 2572; 1884, 17, 456). We are greatly indebted to the Farbwerke vormals Meister, Lucius & Brüning for generously supplying us with all the *o*-nitrobenzaldehyde required for this investigation.



The formation of this substance from *o*-aldehydesuccinanilic acid by internal condensation takes place under the influence of small quantities of alkali, but even when special conditions are observed the yield may vary greatly, and sometimes hydrolysis of the anilic acid may occur to so large an extent that only very small quantities of the carbostyrylacetic acid are produced. The following two processes have been employed with success in the preparation of this substance.

I. Succinanilic acid (5 grams), which must be quite pure, is dissolved in water (100 c.c.) and sodium carbonate (2.5 grams), the solution gradually heated to boiling in a reflux apparatus, and then boiled for four hours. The product is mixed whilst still hot with excess of hydrochloric acid, and allowed to remain for twenty-four hours, when a sandy, crystalline precipitate (3.5 grams) of crude carbostyrylacetic acid separates.

II. Pure succinanilic acid (5 grams) is dissolved in water (150 c.c.) and a slight excess of sodium carbonate; 1 c.c. of a 50 per cent. solution of sodium hydroxide is then added, and the solution heated to boiling in a reflux apparatus for two hours. The hot product is acidified, the precipitate (3.5 grams) of crude carbostyrylacetic acid collected, washed with dilute hydrochloric acid, and drained on porous porcelain.

The crude acid is best purified by dissolving in the minimum quantity of glacial acetic acid, in which it is sparingly soluble, filtering, and then adding half the volume of boiling water, when the pure substance separates as a sandy powder, which, under the microscope, is seen to consist of small prisms:

0.1281 gave 0.3050 CO_2 and 0.0530 H_2O . $\text{C}=64.9$; $\text{H}=4.6$.

0.1411 „ 8.5 c.c. N_2 at 14° and 756 mm. $\text{N}=7.0$.

$\text{C}_{11}\text{H}_9\text{O}_3\text{N}$ requires $\text{C}=65.0$; $\text{H}=4.4$; $\text{N}=6.9$ per cent.

Carbostyryl-3-acetic acid melts and decomposes at about $268\text{--}270^\circ$, and is very sparingly soluble in alcohol, acetone, chloroform, or toluene; it is almost insoluble in cold water, and very sparingly so on boiling, and separates on cooling as a sandy mass of quite colourless crystals.

The *methyl* ester, $\text{C}_{10}\text{H}_8\text{ON} \cdot \text{CO}_2\text{Me}$, is obtained in almost quantitative yield by boiling the acid (5 grams) with methyl alcohol (100 c.c.) and sulphuric acid (10 c.c.), the acid gradually passes

into solution, and, after boiling for three hours in a reflux apparatus on the steam-bath, the solution is allowed to cool, when it becomes filled with a mass of needles of the methyl ester, and a considerable further quantity is precipitated by dilution with two volumes of water. The whole is collected, washed with water, drained on porous porcelain, and recrystallised from methyl alcohol:

0.1435 gave 0.3485 CO_2 and 0.0671 H_2O . $\text{C}=66.2$; $\text{H}=5.2$.

$\text{C}_{12}\text{H}_{11}\text{O}_3\text{N}$ requires $\text{C}=66.3$; $\text{H}=5.1$ per cent.

Methyl carbostyryl-3-acetate melts at 175° , is readily soluble in boiling alcohol or acetone, and crystallises well from both these solvents; it is also readily soluble in hot chloroform or toluene, but sparingly so in light petroleum.

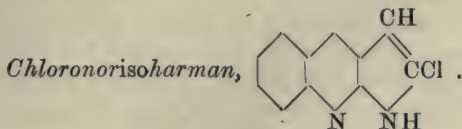
The *amide*, $\text{C}_{10}\text{H}_8\text{ON}\cdot\text{CO}\cdot\text{NH}_2$, may be prepared by heating the methyl ester with a large excess of saturated aqueous ammonia in a sealed tube in the steam-bath for three hours, the whole being then thoroughly shaken and the heating continued for a further six hours. The colourless, granular, crystalline cake is collected, ground up, washed well with water, and the residual, almost pure amide crystallised from dilute acetic acid:

0.1231 gave 0.2969 CO_2 and 0.0591 H_2O . $\text{C}=65.7$; $\text{H}=5.3$.

0.1440 „ 13.7 c.c. N_2 at 14° and 748 mm. $\text{N}=13.9$.

$\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}_2$ requires $\text{C}=65.3$; $\text{H}=4.9$; $\text{N}=13.8$ per cent.

Carbostyryl-3-acetamide melts at about 258° , and decomposes with evolution of gas at $265\text{--}270^\circ$; it is very sparingly soluble in alcohol, acetone, or toluene, and in cold acetic acid, but it dissolves readily in boiling acetic acid, and the solution, diluted with three volumes of water, gradually deposits the pure amide in groups of microscopic needles. The ammoniacal filtrate from the preparation of the amide yields, after boiling away the ammonia and acidifying, a crystalline precipitate of pure carbostyryl-3-acetic acid.



This substance is obtained almost quantitatively when carbostyryl-3-acetamide is heated with phosphoryl chloride. The amide (2 grams), mixed with phosphoryl chloride (5 c.c.), is heated in a test-tube by means of a sulphuric acid bath, when it gradually dissolves with the evolution of hydrogen chloride. After keeping at 80° and shaking until all has dissolved, the temperature is

gradually raised, and most of the excess of phosphoryl chloride distilled out of the test-tube. The dark brown residue is then stirred with water and ice, when a yellow, caseous precipitate separates, which is collected, washed well, drained on porous porcelain, and recrystallised from dilute acetic acid:

0.1341 gave 0.3204 CO_2 and 0.0437 H_2O . $\text{C}=65.1$; $\text{H}=3.6$.

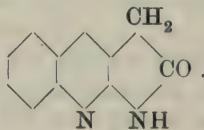
0.1492 „ 0.1054 AgCl . $\text{Cl}=17.5$.

0.1245 „ 15.1 c.c. N_2 at 17° and 753 mm. $\text{N}=14.0$.

$\text{C}_{11}\text{H}_7\text{N}_2\text{Cl}$ requires $\text{C}=65.1$; $\text{H}=3.5$; $\text{N}=13.8$; $\text{Cl}=17.5$ per cent.

Chloronorisoharman melts at 128° to a pale yellow liquid with a green fluorescence. It is readily soluble in boiling alcohol, acetone, chloroform, or benzene, very sparingly so in light petroleum, and separates from a mixture of the latter with benzene in characteristic, lemon-yellow stars; from dilute acetic acid it crystallises in pale yellow leaflets. It dissolves in sulphuric acid, yielding an almost colourless solution, and in concentrated hydrochloric acid with the formation of a salt which is dissociated by water. When a trace is dissolved in boiling quinoline, the solution has an intense green fluorescence very similar to that of fluorescein. It dissolves in dilute methyl-alcoholic potassium hydroxide, and, on warming, a deep crimson solution is produced, but on shaking with air the colour disappears; if water is added to the crimson solution it becomes green, and gradually deposits a crystalline precipitate.

The Lactam (or Lactim) of 2-Aminoquinoline-3-acetic Acid,



This substance is produced when chloronorisoharman (5 grams), dissolved in glacial acetic acid (30 c.c.), is boiled with dry potassium acetate (10 grams); potassium chloride is gradually deposited, and, after two hours, dilution with water causes the lactam to separate as a nearly colourless precipitate. This is collected, washed well, and recrystallised from dilute acetic acid, from which it separates in lemon-yellow, prismatic needles:

0.1468 gave 0.3854 CO_2 and 0.0601 H_2O . $\text{C}=71.6$; $\text{H}=4.4$.

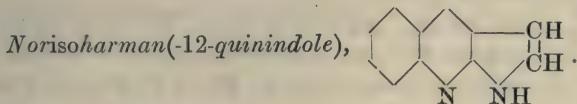
0.1645 „ 0.4342 CO_2 „ 0.0662 H_2O . $\text{C}=72.1$; $\text{H}=4.5$.

0.1293 „ 16.5 c.c. N_2 at 10° and 732 mm. $\text{N}=14.7$.

$\text{C}_{11}\text{H}_8\text{ON}_2$ requires $\text{C}=71.7$; $\text{H}=4.3$; $\text{N}=15.2$ per cent.

The lactam of 2-aminoquinoline-3-acetic acid melts at 235° , and is sparingly soluble in the usual organic solvents, yielding solutions

which have a pale green fluorescence. When the solution in 30 per cent. sulphuric acid is boiled, hydrolysis occurs, and, on adding water, a substance separates, which melts at about 268° , is readily soluble in dilute sodium carbonate, and is therefore doubtless carbostyryl-3-acetic acid.



The difficulty experienced in reducing chloronorisoharman to norisoharman has been referred to in the introduction (p. 1976), and the change was ultimately brought about under the following conditions.

The chloro-derivative (11 grams) is ground to a thin paste with concentrated hydrochloric acid (100 c.c.); granulated tin (30 grams) is then added in small quantities at a time, and the whole repeatedly shaken, when, after about a week, almost the whole of the substance will have dissolved. The tin salt, which will have separated in small quantity, is brought into solution by adding an equal volume of water and heating on the steam-bath; the whole is then filtered, and set aside in the ice-chest to crystallise. The tin salt is then collected, washed, dissolved in hot water, and decomposed by hydrogen sulphide.

After filtering, the filtrate is evaporated to a small bulk, made strongly alkaline with ammonia, when an oil separates, which immediately crystallises, and a further quantity is obtained from the mother liquor by the addition of excess of sodium hydroxide. The substance is collected and recrystallised from light petroleum (b. p. $60-70^{\circ}$), in which norisoharman is sparingly soluble in the cold, and from which it separates in colourless, glistening, feathery groups of needles:

0.0902 gave 0.2584 CO_2 and 0.0406 H_2O . $\text{C}=78.3$; $\text{H}=4.8$.

0.1002 „ 0.2879 CO_2 „ 0.0437 H_2O . $\text{C}=78.3$; $\text{H}=4.8$.

0.1037 „ 15.1 c.c. N_2 at 15° and 745 mm. $\text{N}=16.8$.

$\text{C}_{11}\text{H}_8\text{N}_2$ requires $\text{C}=78.5$; $\text{H}=4.8$; $\text{N}=16.7$ per cent.

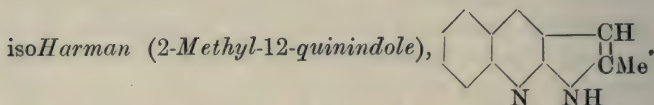
Norisoharman melts at $84-85^{\circ}$, and is readily soluble in the common organic solvents; it dissolves in concentrated sulphuric acid, and the colourless solution has a pale blue fluorescence. It is a powerful base, which dissolves readily even in very dilute hydrochloric acid, and the solution gives, on the addition of mercuric chloride, a voluminous precipitate consisting of long, slender needles. This *mercurichloride* dissolves in much boiling water, and separates on cooling in nodular groups of needles. The *platini-*

chloride, $(C_{12}H_{10}N_2)_2H_2PtCl_2$, separates, on the addition of platinic chloride to the cold dilute solution of the hydrochloride, as a voluminous, drab precipitate, which is sparingly soluble in cold water, but dissolves in much boiling water, and separates, on keeping, as a glistening, pale yellow powder, consisting of well-defined, microscopic prisms:

0.1648 gave 0.2130 CO_2 and 0.0396 H_2O . $C=35.3$; $H=2.4$.

0.3784 „ 0.1007 Pt. $Pt=26.4$.

$(C_{11}H_8N_2)_2H_2PtCl_6$ requires $C=35.4$; $H=2.4$; $Pt=26.2$ per cent.



The first attempts to prepare this substance were by the action of zinc methyl on chloronorisoharman, but, although a variety of conditions were employed, the results were always unsuccessful, and this is the more remarkable since chloronorisoharman is readily soluble in zinc methyl. In one experiment this substance (2 grams), dissolved in zinc methyl (5 grams), was heated in a sealed tube in the steam-bath; the solution became brown, and a brown film formed on the side of the tube.

After an hour the zinc methyl was boiled away, and the residue treated with dilute hydrochloric acid, but no base separated from the filtered solution on the addition of ammonia. The action of magnesium methyl iodide in ethereal solution proved also to be unsuccessful, probably on account of the sparing solubility of chloronorisoharman in that solvent, but ultimately, by employing isoamyl ether instead of ordinary ether, we succeeded in obtaining small quantities of isoharman.

Magnesium (4 grams), covered with pure isoamyl ether, was mixed with methyl iodide (24 grams) and gently heated to start the reaction, and, when this slackened, the whole was heated to boiling, and then chloronorisoharman (5 grams) added all at once. On boiling, the liquid soon clouds, and, after two hours, the product was decomposed by water, the isoamyl ether removed by distillation in steam, the residue mixed with excess of dilute hydrochloric acid and a considerable amount of tar removed by filtration. The filtrate was made strongly alkaline with ammonia, and extracted on the machine with much ether; the ethereal solution was dried over potassium carbonate, evaporated to a small bulk, when, on keeping, nearly pure isoharman (0.2 gram) separated as a brown, crystalline mass. This was dissolved in dilute hydrochloric acid,

filtered from a trace of insoluble, brown impurity, reprecipitated by alkali, and recrystallised from methyl alcohol:

0.1010 gave 0.2914 CO_2 and 0.0527 H_2O . $\text{C}=78.7$; $\text{H}=5.8$.

0.0984 „ 0.2843 CO_2 „ 0.0522 H_2O . $\text{C}=78.9$; $\text{H}=5.9$.

0.1052 „ 14.3 c.c. N_2 at 16° and 752 mm. $\text{N}=15.7$.

$\text{C}_{12}\text{H}_{10}\text{N}_2$ requires $\text{C}=79.1$; $\text{H}=5.5$; $\text{N}=15.4$ per cent.

isoHarman is readily soluble in hot methyl alcohol, and separates on slowly cooling in almost colourless leaflets. It melts at $213\text{--}215^\circ$, and, when heated in small quantities in a test-tube, it sublimes almost without decomposition. The solution in sulphuric acid exhibits a bluish-violet fluorescence. The salts are highly crystalline, and much less soluble than those of *norisoharman*; the hydrochloride crystallises readily from water in slender, yellow needles, and the *mercurichloride* in long needles. The *picrate* is sparingly soluble in most solvents, but may be crystallised from methyl ethyl ketone, from which it separates in yellowish-green needles, which darken above 240° , and melt and decompose at about 253° . The properties of *isoharman* are therefore strikingly similar to those of *harman*, which also sublimes, is readily soluble in alcohol, and dissolves in sulphuric acid to a bluish-violet fluorescent solution. *Harman* melts, however, at 230° , and appears to be more soluble in water than *isoharman*.

Moreover, aqueous solutions of the salts of *harman* exhibit a blue fluorescence, whereas the corresponding salts of *isoharman* do not appear to fluoresce. It is therefore clear that *harman* and *isoharman* are different substances. *

We wish to state that much of the expense of this investigation was defrayed by a grant from the Research Fund of the Royal Society, and to express our thanks to Prof. W. R. Dunstan for kindly obtaining a supply of the seeds of *Peganum harmala*, and to Messrs. Burroughs, Wellcome, and Co. for undertaking the extraction of the alkaloids.

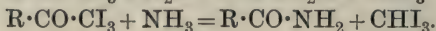
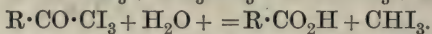
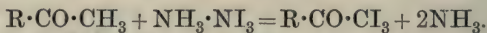
THE UNIVERSITIES OF OXFORD AND MANCHESTER.

CCX.—*The Action of Nitrogen Iodide on Methyl Ketones.*

By FREDERICK DANIEL CHATTAWAY and ROBERT REGINALD BAXTER.

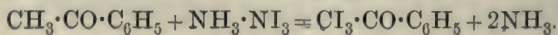
KETONES containing a methyl group react very readily with nitrogen iodide, iodoform, ammonia, an acid, and an amide being produced. In these reactions the methyl group appears first to be completely substituted by iodine, a tri-iodomethyl ketone being formed, which in presence of the ammonia simultaneously set free is hydrolysed to iodoform and an acid, a similar reaction between the substituted ketone and ammonia leading to the formation of iodoform and an amide.

The reactions may be formulated thus:

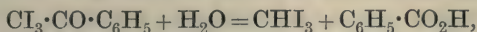


Interaction of Nitrogen Iodide and Acetophenone.

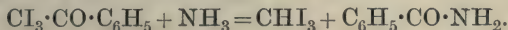
To a quantity of nitrogen iodide suspended in a dilute aqueous solution of ammonia an excess of acetophenone was added, and the mixture vigorously shaken for some hours. The nitrogen iodide gradually disappeared, and the excess of acetophenone, together with the solid product of the action, collected into brown, semi-crystalline lumps. The aqueous layer, having been filtered off through several wetted filter papers, was extracted with ether, and the residue after the first extraction, having been made acid with dilute sulphuric acid, was again extracted with ether. The ethereal extracts were evaporated, and the white solid residues recrystallised from alcohol. The compound extracted from the alkaline liquid proved to be benzamide, and the extract from the acidified residue, benzoic acid. The semi-solid lumps were separated by a filter-pump into a crystalline solid and a heavy brown oil. The solid proved to be iodoform, which was obtained quite pure by one crystallisation from alcohol. The oil consisted of acetophenone, together with a small quantity of some compound containing a large percentage of iodine, possibly the undecomposed tri-iodoacetophenone which must be formed during the reaction; it was, however, obtained in too small an amount to admit of isolation. The reaction probably takes place first by the replacement of hydrogen atoms of the methyl group by iodine, thus:



The intermediate product then reacts with water, thus:



and to a smaller extent with ammonia, thus:



Interaction of Nitrogen Iodide and Acetone.

The action of acetone on nitrogen iodide is very striking, since the black compound in the course of a few minutes is apparently transformed into a bright yellow one. Nitrogen iodide, obtained in a state of fine division by adding a solution of iodine monochloride in hydrochloric acid to strong ammonia, was suspended in a dilute solution of ammonia (20 c.c. of concentrated ammonia in 300 c.c. of water), and about its own weight of acetone added. The flask was shaken at intervals for about fifteen minutes until the black nitrogen iodide had completely disappeared, and its place had been taken by a yellow solid, which proved to be iodoform. The solution was boiled, to expel the excess of acetone and of ammonia, and lead oxide was added to the hot liquid until lead iodide was no longer formed. After cooling, the lead iodide was filtered off, and the filtrate made slightly acid with dilute sulphuric acid. After removing a little lead sulphate, the liquid was distilled, when acetic acid was found in the distillate.

The course of the reaction is undoubtedly similar to that which takes place with acetophenone, but here the acetamide, which probably is formed in small quantity, cannot be isolated.

Preparation of Iodoform.

The method of preparing iodoform ordinarily used in the laboratory, that is, adding iodine to a warm solution of an alkaline carbonate containing ethyl alcohol or acetone, is not at all satisfactory. The yield of iodoform never reaches more than about one-sixth of the weight of iodine used, and may be much less. Part of the iodine lost can, it is true, be recovered from the alkaline mother liquor after separation of the iodoform, although when working on a small scale the amount thus obtained is seldom worth the time and trouble involved.

The interaction of nitrogen iodide and acetone above described affords a means of increasing at least fourfold the yield of iodoform from a given quantity of iodine. By the following procedure about four-fifths of the iodine used can be obtained in the form of iodoform.

A mixture of 40 c.c. of concentrated hydrochloric acid and 4 c.c.

of concentrated nitric acid is gently warmed in an open dish, and 10 grams of finely powdered iodine are gradually added. When the solid iodine has disappeared, the mixture is boiled gently for five minutes, more hydrochloric acid being added to keep up the bulk as the liquid evaporates. No appreciable amount of vapour of iodine monochloride should be given off.

Eighty c.c. of concentrated aqueous ammonia are poured over not less than 200 grams of crushed ice, the mixture is cooled in a freezing machine, and the cooled solution of iodine monochloride is added drop by drop, stirring vigorously during the addition. The nitrogen iodide, separated by a filter-pump and washed several times with concentrated ammonia, is, while still moist and perfectly safe to handle, transferred to a beaker and stirred to a paste with about 20 c.c. of concentrated aqueous ammonia. Ten c.c. of acetone are then immediately added, and the mixture is left, without cooling, until the black nitrogen iodide disappears and a yellow paste of iodoform takes its place. This generally occurs in about five minutes, the temperature of the liquid rising to about 40° . Water is added, the iodoform washed once or twice by decantation, and dissolved in boiling alcohol; usually about 80—100 c.c. of alcohol are needed. A clear, yellow solution is thus obtained, from which, on cooling, 7—8 grams of pure iodoform separate in yellow, hexagonal plates. A further 1—2 grams of iodoform can be obtained by adding water to the alcoholic mother liquor.

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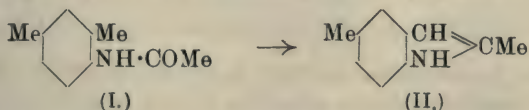
CCXI.—*Researches on the Constitution of Physostigmine. Part III. The Formation of Substituted Indoles from m-4-Xylidine, and the Reduction of 3-Nitro-p-tolylacrylic Acid.*

By ARTHUR HENRY SALWAY.

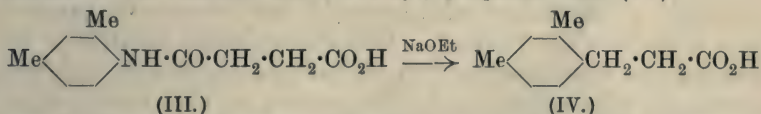
IN continuation of the author's previous investigations (T., 1912, **101**, 978; **103**, 351) on physostigmine (eserine), $C_{15}H_{21}O_2N_3$, some synthetic experiments have been conducted with the object of obtaining a further insight into the constitution of the alkaloid. Although these experiments have not resulted in the synthesis of the desired compounds, and are of no value for the solution of the

problem under consideration, they are not entirely devoid of interest, and it is therefore proposed to place them on record, and to describe the characters of the new compounds which have been prepared.

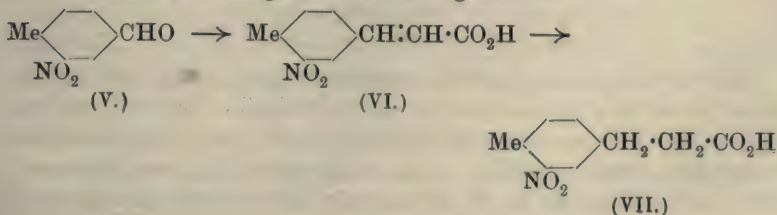
It has recently been shown by Madelung (*Ber.*, 1912, **45**, 1128, 3541) that *o*-toluidides, $C_6H_4 \begin{smallmatrix} < \\ NH \cdot CO \cdot R \\ Me \end{smallmatrix}$, can be converted into indole derivatives, $C_6H_4 \begin{smallmatrix} < \\ NH \\ CH \end{smallmatrix} \geq C \cdot R$, by heating with dry sodium ethoxide. By applying such a reaction to acyl derivatives of *m*-4-xylylidine it was thought that substituted 5-methylindoles might be obtained, and a suitable choice of the acyl radicle would enable one to prepare compounds of service in helping to elucidate the constitution of physostigmine. Consequently it was necessary, in the first place, to ascertain whether the simplest xylylides could be converted by the above method into indole derivatives, and accordingly aceto-*m*-4-xylylidide (I) was investigated in this direction, when a good yield of 2:5-dimethylindole (II) was obtained:



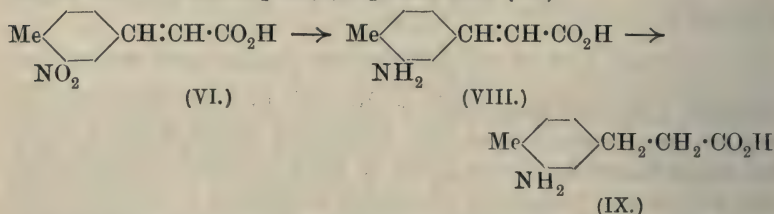
Unfortunately, the reaction was not generally applicable to other derivatives of *m*-4-xylylidine, since the compound of chief interest to the author, namely, 2:4-xylylsuccinamic acid (III), suffers disruption under the influence of dry sodium ethoxide, and the principal product of the reaction was β -2:4-xylylpropionic acid (IV):



The second part of this investigation arose out of an attempt to prepare β -3-nitro-*p*-tolylpropionic acid (VII). For this purpose *p*-tolualdehyde was first nitrated, and the resulting *m*-nitro-*p*-tolualdehyde (V) converted into 3-nitro-*p*-tolylacrylic acid (VI); it was then assumed that the latter would yield the required compound on reduction, according to the following scheme:



It was observed, however, that the nitro-group of 3-nitro-*p*-tolyl-acrylic acid (VI) was more readily attacked by reducing agents than the cinnamyl residue, so that the first product of the reaction was not a substituted propionic acid (VII), but 3-amino-*p*-tolyl-acrylic acid (VIII), which by further reduction then became converted into β -3-amino-*p*-tolylpropionic acid (IX):



Under no condition of reduction investigated by the author was it possible to reduce the 3-nitro-*p*-tolylacrylic acid (VI) without affecting the nitro-group.

EXPERIMENTAL.

I. Preparation of 2:5-Dimethylindole from *m*-4-Xylidine.

In order to ascertain whether *m*-4-xylidine could be converted into 2:5-dimethylindole, a quantity of the former was acetylated, and the resulting acetyl derivative (m. p. 129°; b. p. 170°/10 mm.) heated for a short time at 250—300° with an equal weight of dry sodium ethoxide in the absence of air. After the vigorous reaction which ensued had subsided, water was added, and the mixture distilled in a current of steam. The first portion of the distillate contained xylidine, but subsequently a solid compound began to pass over into the receiver. This was collected separately, and purified by crystallisation from a mixture of benzene and light petroleum, when glistening leaflets melting at 114° were obtained (Found, C=82.7; H=7.7. C₁₀H₁₁N requires C=82.8; H=7.6 per cent.). This substance readily gave the pine-shaving colour reaction typical of indoles, and was evidently identical with 2:5-dimethylindole (compare Raschen, *Annalen*, 1887, **239**, 227). The yield of the latter amounted to 40 per cent. of the acetoxylidide employed in the reaction.

2:4-Xylilsuccinamic Acid (III, p. 1989).

For the preparation of this compound six parts of *m*-4-xylidine were added to a solution of five parts of succinic anhydride in hot chloroform, and the mixture allowed to cool. In a very short time colourless, slender needles of the succinamic acid were deposited, the yield amounting to 80 per cent. of the theoretical. The sub-

stance was collected and purified by crystallisation from chloroform, when it was found to sinter at 160° and to become completely melted at 164° :

0.0965 gave 0.2299 CO_2 and 0.0614 H_2O . $\text{C}=65.0$; $\text{H}=7.1$.

0.1063 required for neutralisation 4.85 c.c. $N/10\text{-KOH}$. Neutralisation Value=256.

$\text{C}_{12}\text{H}_{15}\text{O}_3\text{N}$ requires $\text{C}=65.2$; $\text{H}=6.8$ per cent. Neutralisation Value=254.

2:4-Xylylsuccinamic acid is readily soluble in alcohol, but only moderately so in chloroform, benzene, or hot water. Its methyl ester, prepared by heating the substance for about fifteen minutes * with methyl alcohol saturated with hydrogen chloride, crystallises from a mixture of benzene and light petroleum in colourless needles melting at 107° .

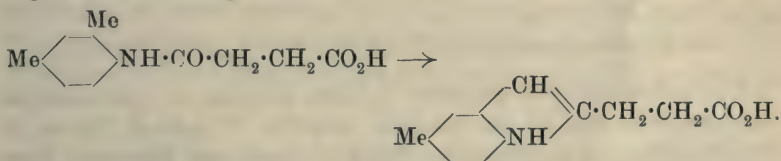
Found: $\text{C}=66.7$; $\text{H}=7.2$.

$\text{C}_{13}\text{H}_{17}\text{O}_3\text{N}$ requires $\text{C}=66.4$; $\text{H}=7.2$ per cent.

Action of Sodium Ethoxide on 2:4-Xylylsuccinamic Acid.

Formation of β -2:4-Xylylpropionic Acid.

The object of this experiment was to ascertain whether 2:4-xylylsuccinamic acid could be converted into an indole derivative according to the following scheme:



Fifty grams of the acid, in convenient portions of 10 grams each, were added to an equal weight of sodium ethoxide in a capacious flask, and the mixture heated for a short time (fifteen minutes) at a temperature of about 300° in the absence of air. The dark-coloured solid thus obtained was digested with water, and the alkaline mixture extracted with ether, which removed some xyloidine and a small quantity (3 grams) of a neutral oil. The alkaline liquid was next filtered from some insoluble resin, and then acidified with dilute hydrochloric acid, when a considerable quantity of acidic substance was precipitated. The mixture was extracted with ether, the ethereal solution being washed, dried, and the solvent removed. The residue thus obtained was found to contain a large proportion of unchanged 2:4-xylylsuccinamic acid, which

* Prolonged heating of this mixture causes hydrolysis, with the formation of xyloidine and succinic acid.

was separated from the other acids present by treatment with cold chloroform (2:4-xylylsuccinamic acid is almost insoluble in this solvent), and filtering the mixture. The filtrate, on evaporation, yielded a residue, which slowly crystallised. The crystalline substance was separated from some oily matter by drying on a porous tile, and was then recrystallised from dilute alcohol, when colourless needles, melting at 106° , were obtained. (Found, $C=74.3$; $H=7.9$. $C_{11}H_{14}O_2$ requires $C=74.2$; $H=7.9$ per cent.)

From the analysis and properties of the above acid there can be no doubt that it is identical with β -2:4-xylylpropionic acid (compare Gattermann, *Annalen*, 1906, 347, 347).

The neutral oil, which had been formed in the above reaction as already described, distilled at $150\text{--}200^{\circ}/15\text{ mm.}$, and was evidently a mixture. It gave a scarlet coloration in contact with a pine shaving which had previously been moistened with concentrated hydrochloric acid, and therefore contained some compound of an indolic character. The yield of this material was, however, too small to enable it to be further investigated.

It is evident from the results of the above experiment that sodium ethoxide at a high temperature effects the disruption of 2:4-xylylsuccinamic acid with the formation of β -2:4-xylylpropionic acid, and no appreciable quantity of a substituted indole is produced.

2:4-Xylylsuccinamide, $C_6H_3Me_2 \cdot NH \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH_2$.

This substance was prepared by the addition of concentrated aqueous ammonia to an alcoholic solution of methyl 2:4-xylylsuccinamate. In a short time the acid amide was deposited from the liquid in glistening leaflets, which melted at 203° and were pure. The compound was also obtained directly from 2:4-xylylsuccinamic acid by heating the latter for a short time with methyl alcohol containing hydrogen chloride, and then adding to the mixture an excess of concentrated aqueous ammonia, when the amide was precipitated in almost a pure condition. The yield of pure substance amounted to 80—90 per cent. of the acid employed in the reaction:

0.1503 gave 0.3598 CO_2 and 0.0987 H_2O . $C=65.3$; $H=7.3$.

$C_{12}H_{16}O_2N_2$ requires $C=65.5$; $H=7.3$ per cent.

2:4-Xylylsuccinamide is readily soluble in alcohol, but only sparingly so in benzene, ethyl acetate, or water. It is also soluble in concentrated hydrochloric acid, but is reprecipitated from this solution on the addition of water. When the substance is heated with aqueous potassium hydroxide, ammonia is rapidly evolved,

with the formation of 2:4-xylylsuccinamic acid, which is further resolved, on prolonged heating with the alkali, into xylidine and succinic acid.

An attempt was made to convert the above amide into an indole derivative by heating with sodium ethoxide in a manner similar to that described in connexion with 2:4-xylylsuccinamic acid, but without success, since the only compounds that could be isolated from the reaction mixture were xylidine and 2:4-xylylsuccinamic acid.

II. Reduction of 3-Nitro-*p*-tolylacrylic Acid (VI, p. 1989).

The 3-nitro-*p*-tolylacrylic acid required for these experiments was prepared from *p*-tolualdehyde in the manner already described by Hanzlik and Bianchi (*Ber.*, 1899, **32**, 1288, 2285). In order to ascertain, in the first place, whether reduction could be effected by means of sodium amalgam, 800 grams of the latter (4 per cent. Na) were added in small quantities, with continuous mechanical stirring, to a solution of the acid in dilute sodium hydroxide. After the amalgam had been completely decomposed, the alkaline liquid was filtered, then acidified, and the acidic substance, which was precipitated, was collected. The greater part of the latter was found to consist of unchanged material, but a small quantity of an indefinite acid of high melting point was isolated, which appeared to be formed from the original acid by polymerisation under the influence of the alkali. No evidence was obtained of the formation of any β -3-nitro-*p*-tolylpropionic acid (VII, p. 1989) in the reaction.

3-Amino-*p*-tolylacrylic Acid (VIII, p. 1990).

This compound was obtained as the first reduction product of 3-nitro-*p*-tolylacrylic acid when the latter was heated for a short time at 100° with an excess of hydriodic acid (D 1·7) and red phosphorus. As soon as the vigorous initial reaction had subsided, water was added, and the mixture filtered to remove the red phosphorus. The filtrate, on concentration, yielded well-formed crystals of a hydriodide, which were collected and dissolved in a little water. Aqueous sodium carbonate was then cautiously added to the solution, when the amino-acid was deposited as a yellow precipitate. It was purified by crystallisation from alcohol, and thus obtained in lemon-yellow, elongated needles, melting at 184°:

0·0984 gave 0·2443 CO₂ and 0·0548 H₂O. C=67·7; H=6·2.

C₁₀H₁₁O₂N requires C=67·8; H=6·2 per cent.

It is evident from the above analysis that the cinnamyl residue

has remained intact during the reduction, whilst the nitro-group has been converted into an amino-group with the formation of 3-amino-*p*-tolylacrylic acid.

3-Amino-*p*-tolylacrylic acid is very sparingly soluble in chloroform, ether, or benzene, and moderately so in hot water or hot alcohol. It separates from the latter solvents, on cooling, in well-formed needles. It possesses both acid and basic properties, and is converted by further reduction into the following compound.

β-3-Amino-*p*-tolylpropionic Acid (IX, p. 1990).

This compound was prepared by heating 3-nitro-*p*-tolylacrylic acid for two hours with ten parts of hydriodic acid (D 1·7) and one part of red phosphorus. Water was then added to the reaction product, the mixture subsequently filtered, and the filtrate concentrated to a small volume, when colourless crystals of a hydriodide were deposited. These were collected, dissolved in a little water, and the free amino-acid was then precipitated by the addition of the requisite quantity of sodium carbonate. The substance was purified by crystallisation from dilute alcohol, when it was obtained in stellar aggregates of colourless needles, melting at 142–143°:

0·0952 gave 0·2340 CO₂ and 0·0650 H₂O. C=67·0; H=7·6.

C₁₀H₁₃O₂N requires C=67·0; H=7·3 per cent.

β-3-Amino-*p*-tolylpropionic acid is readily soluble in alcohol or hot water, but only sparingly so in ether, chloroform, or benzene. Its *diacetyl* derivative, NAc₂·C₆H₃Me·CH₂·CH₂·CO₂H, prepared by heating the amino-acid with acetic anhydride for a few hours, and then pouring the mixture into water, crystallises from the latter solvent in glistening leaflets, which sinter at 122° and melt at about 160°:

0·0872 gave 0·2044 CO₂ and 0·0507 H₂O. C=63·9; H=6·5.

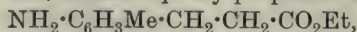
C₁₄H₁₇O₄N requires C=63·9; H=6·5 per cent.

The *monoacetyl* derivative, NHAc·C₆H₃Me·CH₂·CH₂·CO₂H, obtained by dissolving the diacetyl compound in hot dilute (*N*/10) hydrochloric acid, and allowing the solution to cool, crystallises in colourless, slender needles, melting at 200°. It can also be prepared by heating the amino-acid, for a few minutes only, with acetic anhydride:

0·1028 gave 0·2459 CO₂ and 0·0628 H₂O. C=65·2; H=6·8.

C₁₂H₁₅O₃N requires C=65·2; H=6·8 per cent.

The *ethyl* ester of *β*-3-amino-*p*-tolylpropionic acid,



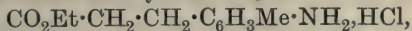
prepared from the acid by treatment with hot alcohol in the

presence of hydrogen chloride, is a liquid which distils at $208^{\circ}/30$ mm., and possesses a pleasant, nut-like odour:

0.1008 gave 0.2564 CO_2 and 0.0758 H_2O . $\text{C}=69.4$; $\text{H}=8.4$.

$\text{C}_{12}\text{H}_{17}\text{O}_2\text{N}$ requires $\text{C}=69.6$; $\text{H}=8.2$ per cent.

The above-described ester yields a *hydrochloride*,



which crystallises from a mixture of ether and alcohol in small, colourless prisms, melting at $115-117^{\circ}$.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CCXII.—*The Action of Chlorine on m-Iodoaniline and on m-Bromoaniline.*

By HAMILTON McCOMBIE and PERCY JAMES WARD.

THE marked influence of the presence of a hydroxyl group in the benzene nucleus on the tervalency of the iodine atom, which has been studied by Brazier and McCombie (T., 1912, **101**, 948) and by King and McCombie (this vol., p. 220), led the authors to consider the influence which other groups (especially such as possess considerable partial valency) exert on the iodine atom, and the first group which was selected for this purpose was the amino-group.

The action of chlorine on aromatic iodo-compounds which contain the amino-group seems to have been studied only very slightly. Willgerodt and Simonis (*Ber.*, 1906, **39**, 273) found that 4-iodo-*m*-toluidine ($\text{Me}=1$), when acted on by chlorine in chloroform solution, yielded a very unstable iododichloride, together with other higher chlorination products. Hofmann (*Annalen*, 1848, **67**, 65) noticed that *p*-iodoaniline with chlorine gave 2:4:6-trichloroaniline very readily. This result has been confirmed by the authors, who have found that *p*-iodoaniline does not yield an iododichloride in any solvent, even when the solution is cooled in a freezing mixture—iodine is liberated immediately. The only statement which the authors have been able to find with reference to the action of chlorine on *m*-iodoaniline is one by Willgerodt and Wikander (*Ber.*, 1907, **40**, 4068), who considered that they had obtained an unstable iododichloride. On passing chlorine into a chloroform solution of *m*-iodoaniline, these experimenters obtained a dark red powder which, they state, decomposed rapidly, yielding

a product they were unable to analyse. By treatment with sodium hydroxide, *m*-iodoaniline was regenerated, from which fact they concluded that the original substance was an iododichloride. It seems probable from our work that these chemists had in their hands merely an impure specimen of *m*-iodoaniline hydrochloride.

When a 3 per cent. solution of *m*-iodoaniline in glacial acetic acid was subjected to the action of chlorine at the ordinary temperature, a quantitative yield of 2:4:6-trichloro-3-iodoaniline was obtained. On no occasion was the formation of an iododichloride observed. If concentrated acetic acid solutions were employed, some iodine was liberated, and a considerable quantity of *m*-iodoaniline hydrochloride was deposited. When carbon tetrachloride and chloroform were employed as solvents, it was impossible to prepare much of the chlorination product, owing to the precipitation of the hydrochloride of the original iodoaniline.

The constitution of 2:4:6-trichloro-3-iodoaniline was established by heating the substance on a water-bath with excess of alcoholic ethyl nitrite and a little concentrated hydrochloric acid. By this means the amino-group was replaced by hydrogen, and there resulted 2:4:6-trichloriodobenzene (Jackson and Gazzolo, *Amer. Chem. J.*, 1890, **22**, 52; Hantzsch, *Ber.*, 1897, **30**, 2354).

Analogous compounds to 2:4:6-trichloro-3-iodoaniline, produced by the chlorination of *m*-iodoaniline in this way, are obtained by the chlorination of the corresponding chloro- and bromo-compounds (see Beilstein and Kurbatoff, *Annalen*, 1877, **196**, 236; Orton and Reed, *T.*, 1907, **91**, 1552).

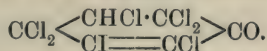
Some interesting examples of the influence of substituents on the course of a reaction were encountered in dealing with 2:4:6-trichloro-3-iodoaniline. It was found that no hydrochloride was produced by saturating an alcoholic solution with hydrogen chloride. Benzoylation in the presence of sodium hydroxide was without effect on the compound, but in the presence of pyridine the reaction proceeded quite smoothly. In this respect the behaviour is very similar to that of the halogen substituted phenols prepared by Brazier and McCombie (*loc. cit.*). Orton and Reed (*loc. cit.*) obtained some unexpected results when acetylating 2:4:6-trichloro-3-bromoaniline. When this substance was heated with acetic anhydride for several hours, a diacetyl derivative was obtained. When, however, the acetylation was conducted by warming the compound with acetyl chloride in a sealed tube, the monoacetyl derivative was produced. Similar results have been obtained in the case of 2:4:6-trichloro-3-iodoaniline.

When *m*-iodoaniline is converted into acyl derivatives, the partial valency of the amino-group is neutralised to a certain extent, and

these acyl derivatives show tendencies for the iodine to become tervalent. In these cases iododichlorides are produced, but they prove to be very unstable. Willgerodt and Wikander (*loc. cit.*) have described the chlorination of *m*-iodoacetanilide in an ice-cold chloroform solution, and state that an iododichloride was formed, but the figures they obtained in the analysis of this compound were very high. On repeating this work, the authors have found that an iododichloride was precipitated, but that it was very unstable, and decomposed with evolution of hydrogen chloride. When chlorine was passed into a hot glacial acetic acid solution of *m*-iodoacetanilide, 2:4:6-trichloro-3-iodoacetanilide was obtained. The constitution of this compound was confirmed by its identity with the substance produced on acetylating 2:4:6-trichloro-3-iodoaniline.

Somewhat similar results were obtained in dealing with the benzoyl derivative of *m*-iodoaniline. In a cold solution an unstable iododichloride was produced, whilst in a warm solution benzoyl-2:4-dichloro-5-iodoaniline resulted.

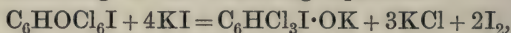
If, at ordinary room temperature, chlorine is passed into an acetic acid solution of *m*-iodoaniline for several hours, the 2:4:6-trichloro-5-iodoaniline, which is at first precipitated, disappears slowly, and a clear, yellow liquid is obtained, which deposits a quantity of ammonium chloride. When the acetic acid is removed, there is obtained a crystalline substance mixed with a dark red oil. This crystalline substance, on further examination, is found to be 2:2:3:4:4:6-hexachloro-5-iodo- Δ^5 -cyclohexenone,



This same compound may be obtained also by chlorinating a suspension of *m*-iodoaniline hydrochloride in acetic acid or by chlorinating *m*-iodoaniline in acetic acid at the temperature of the water-bath. It is interesting to notice that in the formation of the compound the action of the chlorine has been to remove the amino-group, but the iodine atom is left untouched. Considering that in the case of *p*-iodoaniline the first action of chlorine, even in a cold solution, is to displace the iodine, it is readily seen that the position of the iodine atom in the aniline molecule is of great importance in relation to the strength of its union to the carbon atom.

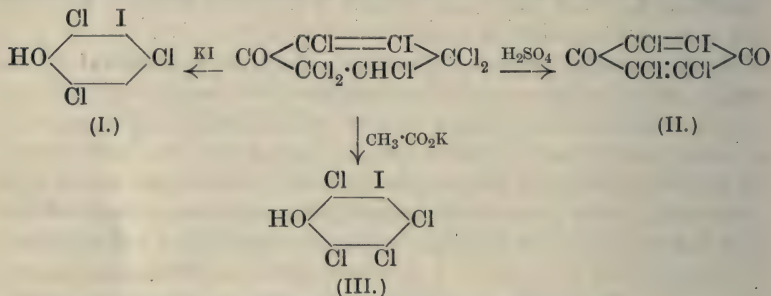
The constitution to be assigned to this ultimate chlorination product of *m*-iodoaniline is based on the following experimental facts: (1) Analyses show that there are six chlorine atoms and one iodine. As the compound is produced by the chlorination of 2:4:6-trichloro-3-iodoaniline, there must be chlorine atoms in

position 2, 4, and 6, and an iodine atom in position 3. Further, there must be one double bond in the molecule. (2) The compound, when heated with concentrated sulphuric acid on the water-bath, yielded 2:3:6-trichloro-5-iodo-*p*-benzoquinone (II). (3) The substance liberated iodine from potassium iodide, with the formation of 2:4:6-trichloro-3-iodophenol (I), and the reaction was found to proceed according to the following equation:

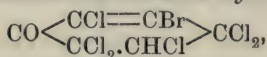


From this reaction it follows that there must be a hydrogen atom in the molecule of the substance, and this hydrogen atom must be in the meta-position with respect to the iodine atom.

(4) 2:3:4:6-Tetrachloro-5-iodophenol (III) was produced by boiling the substance with potassium acetate in the presence of acetic acid. From this reaction it follows that there must be a chlorine atom in position 3, as well as a hydrogen atom. A summary of these reactions is given in the accompanying diagram:



2:2:3:4:4:6-Hexachloro-5-bromo- Δ^5 -cyclohexenone,



was obtained in exactly the same way by the chlorination of *m*-bromoaniline, and its rearrangements with the same reagents as are employed for the iodo-compound show that it is constituted similarly to that substance. Thus, this bromo-compound, when acted on by concentrated sulphuric acid, yielded 2:3:6-trichloro-5-bromo-*p*-benzoquinone; with potassium iodide there resulted 2:4:6-trichloro-3-bromophenol, and treatment with potassium acetate in presence of acetic acid resulted in the formation of 2:3:4:6-tetrachloro-5-bromophenol.

It is interesting to note, also, that very similar results were obtained by Zincke and Shaum (*Ber.*, 1894, **27**, 548) by the action of chlorine on *m*-chloroaniline.

These chemists obtained two products in this reaction, namely, 2:3:4:4:5:6:6-heptachloro- Δ^2 -cyclohexenone and 2:2:3:4:5:6:6-heptachloro- Δ^3 -cyclohexenone.

EXPERIMENTAL.

The *m*-iodoaniline used in these experiments was prepared from *m*-nitroaniline according to the method described by Baeyer (*Ber.*, 1905, **38**, 2761), but this method was modified in the second stage of the reaction, namely, the conversion of the *m*-iodonitrobenzene into *m*-iodoaniline. This reduction was effected by Baeyer in the presence of methylated spirit, and it was found that after neutralisation and steam distillation, considerable quantities of *m*-iodoaniline were dissolved in the methylated spirit, and could not be recovered by dilution with water. Our modification consisted in distilling off the methylated spirit before neutralising the solution.

m-Iodoaniline Hydrochloride, $C_6H_4I \cdot NH_2 \cdot HCl$.

This compound was prepared by passing a stream of dry hydrogen chloride into a solution of *m*-iodoaniline in ethyl alcohol. Most of the solvent was then allowed to evaporate, and the hydrochloride was obtained in large, white leaflets, which melted at 260° :

0.1000 gave 0.1488 $AgCl + AgI$.

C_6H_5NI, HCl requires $AgCl + AgI = 0.1481$.

A suspension of *m*-iodoaniline hydrochloride in glacial acetic acid was chlorinated for about an hour. The hydrochloride gradually disappeared, hydrogen chloride was evolved, and the solution was found to contain 2:3:3:4:4:6-hexachloro-5-iodo- Δ^5 -cyclohexenone, melting at 104° .

Action of Chlorine on m-Iodoacetanilide: Preparation of 2:4:6-Trichloro-3-iodoacetanilide.

m-Iodoacetanilide, which was prepared by heating *m*-iodoaniline with acetic anhydride and a drop of acetyl chloride, was dissolved in glacial acetic acid, and the solution heated to the boiling point. A stream of chlorine was passed through the solution, and, when the evolution of hydrogen chloride had ceased, the liquid was concentrated to a small bulk. The white crystals which appeared were separated and recrystallised from a mixture of acetic acid and water, when they consisted of short needles, melting at 204° :

0.0941 gave 0.1715 $AgCl + AgI$.

$C_8H_5ONCl_3I$ requires $AgCl + AgI = 0.1718$.

2:4:6-Trichloro-3-iodoacetanilide is moderately soluble in acetic acid or light petroleum, very soluble in ethyl alcohol, and only sparingly so in acetone.

Benzoyl-m-iodoaniline, C₆H₄I·NHBz.

This compound was prepared by benzylation in presence of sodium hydroxide. When recrystallised twice from methylated spirit, it separated in slender, white needles, melting at 156—157°:

0.1000 gave 0.0719 AgI. $I = 38.85$.

$C_{13}H_{10}ONI$ requires $I = 39.32$ per cent.

Action of Chlorine on Benzoyl-m-iodoaniline: Preparation of Benzoyl-2:4-dichloro-5-iodoaniline.

On passing chlorine into a solution of benzoyl-*m*-iodoaniline in glacial acetic acid, an unstable iododichloride was at first precipitated. On boiling the solution, this unstable compound dissolved, and the passage of chlorine through the hot solution was continued. The solution was concentrated, and the short, white needles which appeared were separated and recrystallised from a mixture of glacial acetic acid and water, when the product was found to melt at 142°:

0.0708 gave 0.0932 AgCl + AgI.

$C_{13}H_8ONCl_2I$ requires AgCl + AgI = 0.0943.

Action of Chlorine on m-Iodoaniline: Preparation of 2:4:6-Trichloro-3-iodoaniline.

Ten grams of powdered *m*-iodoaniline were dissolved in 350 c.c. of glacial acetic acid, and a stream of chlorine was led into the solution. After a few minutes the liquid became dark green, then the colour changed to pale yellow, and fine, white crystals began to separate, accompanied by a rapid evolution of hydrogen chloride. The solution was then cooled, and the contents of the beaker were found to be almost solid. The crystals were separated, and the liquid subjected to the further action of chlorine, which process was continued until no more solid separated. The crude solid was washed with dilute sodium carbonate solution, and was found to weigh 12—13 grams. It was recrystallised from methyl alcohol, and separated in short, slender needles, melting at 88°:

0.1380 gave 0.2837 AgCl + AgI.

$C_6H_3NCl_3I$ requires AgCl + AgI = 0.2847.

2:4:6-Trichloro-3-iodoaniline is sparingly soluble in acetic acid, methyl alcohol, or light petroleum, and readily so in ethyl alcohol or acetone. The crystals assume a pink tinge after being kept for a short period. When subjected to the action of chlorine for a long time at the ordinary temperature or a shorter time

at the temperature of the water-bath, this compound yields 2:2:3:4:4:6-hexachloro-5-iodo- Δ^5 -cyclohexenone. 2:4:6-Trichloro-3-iodoaniline was boiled on the water-bath with an excess of alcoholic ethyl nitrite and a little concentrated hydrochloric acid; the alcohol was distilled off, and the residue was recrystallised from a mixture of glacial acetic acid and water, when a compound melting at 55° was obtained. This substance proved to be 2:4:6-trichloriodobenzene, previously described by Jackson and Gazzolo (*loc. cit.*) and by Hantzsch (*loc. cit.*). This reaction establishes the constitution of this chlorination product of *m*-iodoaniline.

Benzoyl-2:4:6-trichloro-3-iodoaniline.

It was found that 2:4:6-trichloro-3-iodoaniline could not be converted into the benzoyl derivative by the action of benzoyl chloride in the presence of sodium hydroxide, so that recourse was had to the pyridine method of benzylation.

One gram of 2:4:6-trichloro-3-iodoaniline was dissolved in pyridine, and 0.5 gram of pure benzoyl chloride was added carefully. The solution was allowed to remain overnight, and was then poured into dilute hydrochloric acid. After several hours the precipitated product solidified, and, after separation, was washed with warm methyl alcohol, in which it is only sparingly soluble; after three recrystallisations from ethyl alcohol the benzoyl derivative was obtained in glistening, white leaflets, which melted at 229° :

0.0910 gave 0.1408 AgCl + AgI.

$C_{13}H_7ONCl_3I$ requires AgCl + AgI = 0.1420.

Benzoyl-2:4:6-trichloro-3-iodoaniline is only sparingly soluble in acetone, but is moderately so in acetic acid; it is quite insoluble in benzene.

*Preparation of 2:4:6-Trichloro-3-iodoacetanilide from
2:4:6-Trichloro-3-iodoaniline.*

This compound was prepared by heating 2:4:6-trichloro-3-iodoaniline with an excess of acetyl chloride in a sealed tube on the water-bath. After being heated for fifteen minutes the tube was opened, the excess of acetyl chloride removed in a current of air, and the residue when recrystallised from a mixture of acetic acid and water proved identical with the product obtained by the chlorination of *m*-iodoacetanilide.

Chlorination of a Hot Solution of m-Iodoaniline: Preparation of 2:2:3:4:4:6-Hexachloro-5-iodo- Δ^5 -cyclohexenone.

Ten grams of *m*-iodoaniline were dissolved in 350 c.c. of glacial acetic acid, the solution was warmed for a few minutes on a water-bath, and a stream of chlorine was passed through the solution. After a short time hydrogen chloride was evolved readily, and white crystals of ammonium chloride were deposited. When the chlorination had proceeded for about two hours, the evolution of hydrogen chloride had practically ceased, and the solution was then evaporated to dryness. The residue was washed with water to remove the ammonium chloride produced in the reaction, and there resulted about 18 grams of a crude oily product, with an odour strongly resembling that of camphor. This product, when recrystallised from glacial acetic acid, separated in large, transparent prisms, which melted at 104° :

0.1023 gave $0.2631 \text{ AgCl} + \text{AgI}$.

$\text{C}_6\text{HOC}_l_6\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.2614$.

2:2:3:4:4:6-*Hexachloro-5-iodo- Δ^5 -cyclohexenone* is moderately soluble in methyl and ethyl alcohols, sparingly so in glacial acetic acid, and very soluble in acetone.

The method of preparation described above was not always satisfactory. In some cases the reaction proceeded too vigorously, resulting in the liberation of a large amount of iodine, probably producing a fair quantity of 2:3:4:4:5:6:6-heptachloro- Δ^2 -cyclohexenone, from which it is a matter of great difficulty to separate the iodo-compound.

If the chlorination was conducted in a cold solution, no iodine was liberated. Under these conditions the reaction required two days for completion, and a considerable quantity of the oily by-product was obtained.

When this compound was treated with concentrated sulphuric acid, it yielded trichloriodobenzoquinone; with potassium iodide, it yielded trichloriodophenol; and with potassium acetate, tetrachloriodophenol. These reactions established its constitution.

2:4:6-Trichloro-3-iodophenol.

Five grams of 2:2:3:4:4:6-hexachloro-5-iodo- Δ^5 -cyclohexenone were dissolved in warm glacial acetic acid, and 10 grams of powdered potassium iodide were added. Liberation of iodine commenced immediately, and when the mixture had been warmed on the water-bath for half an hour, the reaction was complete. The iodine was removed by the addition of sodium hydrogen

sulphite, and the phenol was separated and recrystallised from a mixture of glacial acetic acid and water. It crystallised in white, silky needles, melting at 102° :

0.0879 gave $0.1826 \text{ AgCl} + \text{AgI}$.

$\text{C}_6\text{H}_2\text{OCl}_3\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.1808$.

2:4:6-Trichloro-3-iodophenol is moderately soluble in ethyl and methyl alcohols, and readily so in acetic acid.

The *acetyl* derivative, $\text{C}_6\text{H}_2\text{Cl}_3\text{I} \cdot \text{OAc}$, was prepared by the action of acetic anhydride on 2:4:6-trichloro-3-iodophenol. It crystallises from a concentrated alcoholic solution in small leaflets, melting at 87° :

0.0555 gave $0.1034 \text{ AgCl} + \text{AgI}$.

$\text{C}_6\text{H}_4\text{O}_2\text{Cl}_3\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.1010$.

The *benzoyl* derivative, $\text{C}_6\text{H}_2\text{Cl}_3\text{I} \cdot \text{OBz}$, was prepared by the pyridine method, and when recrystallised from ethyl alcohol separated in small needles, which melted at $136\text{--}138^{\circ}$:

0.0620 gave $0.0967 \text{ AgCl} + \text{AgI}$.

$\text{C}_{13}\text{H}_6\text{O}_2\text{Cl}_3\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.0965$.

This derivative is readily soluble in acetone, and sparingly so in ethyl and methyl alcohols.

2:3:6-Trichloro-5-iodo-p-benzoquinone.

This compound was prepared by heating hexachloroiodocyclohexenone cautiously with concentrated sulphuric acid on a water-bath for about four hours. The solution was poured into water; the product, after separation, was washed first with water, and then with methyl alcohol:

0.0460 gave $0.0920 \text{ AgCl} + \text{AgI}$.

$\text{C}_6\text{O}_2\text{Cl}_3\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.0907$.

2:3:6-Trichloro-5-iodo-p-benzoquinone possesses a deep reddish-yellow colour, and can be sublimed at about 150° ; it melts indefinitely at about 280° . When attempts were made to recrystallise it from methyl alcohol it was found that decomposition took place. In other organic solvents it was practically insoluble.

2:3:4:6-Tetrachloro-5-iodophenol.

Four grams (1 mol.) of hexachloroiodocyclohexenone were heated on the water-bath with three grams (3 mols.) of potassium acetate in the presence of acetic acid. After two hours the mixture was poured into water, the phenol was separated, and the residue washed well with water, and then recrystallised three times from

light petroleum, in which it is only sparingly soluble. It was obtained in long, white needles, melting at 169° :

0.0596 gave 0.1359 $\text{AgCl} + \text{AgI}$.

$\text{C}_6\text{HOCl}_4\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.1347$.

2 : 3 : 4 : 6-*Tetrachloro-5-iodophenol* is moderately soluble in acetic acid, and also in methyl and ethyl alcohols.

The *acetyl* derivative, $\text{C}_6\text{HCl}_4\text{I} \cdot \text{OAc}$, was prepared by heating tetrachloroiodophenol with acetic anhydride. It was crystallised from ethyl alcohol, from which it separated in glistening, short needles, melting at $140\text{--}141^{\circ}$:

0.0477 gave 0.0967 $\text{AgCl} + \text{AgI}$.

$\text{C}_8\text{H}_3\text{O}_2\text{Cl}_4\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.0964$.

The *acetyl* derivative is sparingly soluble in ethyl alcohol, and moderately so in methyl alcohol.

The *benzoyl* derivative, $\text{C}_6\text{HCl}_4\text{I} \cdot \text{OBz}$, was prepared by the pyridine method, and when recrystallised from ethyl alcohol separated in small, white prisms, melting at $175\text{--}176^{\circ}$:

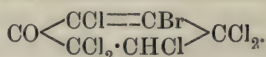
0.0609 gave 0.1060 $\text{AgCl} + \text{AgI}$.

$\text{C}_{13}\text{H}_5\text{O}_2\text{Cl}_4\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.1066$.

This compound is only sparingly soluble in methyl and ethyl alcohols, insoluble in light petroleum, and readily soluble in acetone.

Chlorination of a Hot Solution of m-Bromoaniline: Preparation of

2 : 2 : 3 : 4 : 4 : 6-*Hexachloro-5-bromo- Δ^5 -cyclohexenone*.



This compound was prepared in a manner similar to that employed for the corresponding iodo-compound. When crystallised from glacial acetic acid, it forms transparent prisms, melting at 106° :

0.0923 gave 0.2558 $\text{AgCl} + \text{AgBr}$.

$\text{C}_6\text{HOCl}_6\text{Br}$ requires $\text{AgCl} + \text{AgBr} = 0.2534$.

The solubilities of this bromo-compound were of the same order as those of the iodo-compound, thus, it is moderately soluble in methyl and ethyl alcohols, and sparingly so in glacial acetic acid.

2 : 4 : 6-*Trichloro-3-bromophenol*.

Two grams of hexachlorobromocyclohexenone were treated with 6 grams of powdered potassium iodide in the presence of acetic acid by the method used for the preparation of trichloroiodophenol. The product was crystallised from a mixture of acetic acid and

water, from which it separated in white, silky needles, melting at 61° :

0.0936 gave $0.2115 \text{ AgCl} + \text{AgBr}$.

$\text{C}_6\text{H}_2\text{OCl}_3\text{Br}$ requires $\text{AgCl} + \text{AgBr} = 0.2095$.

2:4:6-Trichloro-3-bromophenol is moderately soluble in methyl and ethyl alcohols and in glacial acetic acid.

The *acetyl* derivative, $\text{C}_6\text{HCl}_3\text{Br}\cdot\text{OAc}$, was obtained by the action of acetic anhydride and crystallised in small leaflets, melting at 70° :

0.0644 gave $0.1266 \text{ AgCl} + \text{AgBr}$.

$\text{C}_8\text{H}_4\text{O}_2\text{Cl}_3\text{Br}$ requires $\text{AgCl} + \text{AgBr} = 0.1252$.

The *benzoyl* derivative, $\text{C}_6\text{HCl}_3\text{Br}\cdot\text{OBz}$, was prepared in pyridine solution, and when recrystallised from ethyl alcohol melted at 102° :

0.0447 gave $0.0732 \text{ AgCl} + \text{AgBr}$.

$\text{C}_{13}\text{H}_6\text{O}_2\text{Cl}_3\text{Br}$ requires $\text{AgCl} + \text{AgBr} = 0.0727$.

2:3:6-Trichloro-5-bromo-p-benzoquinone.

This was prepared by heating hexachlorobromocyclohexenone with concentrated sulphuric acid for three hours on a water-bath. The acid liquid was poured into water, and the yellow product was crystallised from much methyl alcohol, in which it is only sparingly soluble. It was obtained in bright yellow leaflets, melting at 292° (Found, $\text{AgCl} + \text{AgBr} = 0.1798$. Calculated, 0.1774). This substance has been described by several investigators, notably by Levy and Schultz (*Annalen*, 1881, **210**, 162), who prepared it by the action of bromine on trichlorobenzoquinone.

2:3:4:6-Tetrachloro-5-bromophenol.

Hexachlorobromocyclohexenone (1 mol.), dissolved in acetic acid, was treated with potassium acetate (3 mols.) in a manner similar to that employed in the case of the corresponding iodo-compound. It was crystallised from light petroleum, when it separated in white needles, melting at 192° :

0.0531 gave $0.1324 \text{ AgCl} + \text{AgBr}$.

$\text{C}_6\text{HOCl}_4\text{Br}$ requires $\text{AgCl} + \text{AgBr} = 0.1300$.

The *acetyl* derivative, $\text{C}_6\text{Cl}_4\text{Br}\cdot\text{OAc}$, was obtained by means of acetic anhydride, and when crystallised from ethyl alcohol yielded slender, glistening needles, melting at 144° :

0.0610 gave $0.1334 \text{ AgCl} + \text{AgBr}$.

$\text{C}_8\text{H}_3\text{O}_2\text{Cl}_4\text{Br}$ requires $\text{AgCl} + \text{AgBr} = 0.1317$.

This substance is only sparingly soluble in ethyl and methyl alcohols, but is readily soluble in acetone.

The *benzoyl* derivative, $\text{C}_6\text{Cl}_4\text{Br}\cdot\text{OBz}$, was prepared in pyridine

solution, and crystallised from methyl alcohol in small, white prisms, melting at 169° :

0.0505 gave $0.0921 \text{ AgCl} + \text{AgBr}$.

$\text{C}_{13}\text{H}_5\text{O}_2\text{Cl}_4\text{Br}$ requires $\text{AgCl} + \text{AgBr} = 0.0927$.

This substance is sparingly soluble in methyl and ethyl alcohols, but dissolves readily in acetone.

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CCXIII.—*The Constituents of Senna Leaves.*

By FRANK TUTIN.

SENNA leaves have in the past been the subject of numerous investigations, but until recently little information has been obtained regarding the definite compounds present in them. Most of the investigators have recorded the isolation of "chrysophanic acid" and the "cathartic acid" of Dragendorff—a product to which the purgative action of the drug has been attributed—but which for some time has been recognised as an indefinite mixture of substances.

The most recent investigation of importance on this subject is that by Tschirch and Hiepe (*Arch. Pharm.*, 1900, **238**, 427), where a detailed mention of the previous literature will be found. These investigators described the isolation of the following products: A crystalline substance, $\text{C}_{14}\text{H}_{10}\text{O}_5$; "sennarhamnetin"; "anthraglucosennin"; "senna-emodin"; "sennachrysophanic acid"; "sennaisoemodin," and amorphous "sennanigrin." No melting point was recorded for the "substance, $\text{C}_{14}\text{H}_{10}\text{O}_5$," and in view of the results of the present investigation it would appear probable that it was a mixture of aloe-emodin and rhein. The latter substance, which has now been isolated from senna, had previously been known to occur only in rhubarb. With regard to the "sennarhamnetin," Tschirch and Hiepe record no analysis, and merely state that the product in question did not melt at 260° . It is now shown, however, that the flavone product present in various specimens of senna leaves consists either of kaempferol (m. p. 274°) or of a mixture of the latter with isorhamnetin (m. p. 302°). The "anthraglucosennin" of the last-mentioned authors would appear to have been a mixture of the glucosides of rhein

and aloe-emodin, the latter compound being the so-called "senna-emodin." "Sennanigrin" is an amorphous, indefinite product, and the occurrence of "sennachrysophanic acid" (chrysophanol) and of "sennaisoemodin"—for which no melting point is given—cannot be confirmed.

With regard to the alleged occurrence of chrysophanic acid in senna, it is stated by Tschirch and Hiepe (*loc. cit.*, p. 435) that the product obtained by them was free from methoxyl, and melted at 171—172°. In subsequent communications, however (Tschirch and Bromberger, *Arch. Pharm.*, 1911, **249**, 222, and Tschirch and Weil, *ibid.*, 1912, **250**, 26), it is emphasised that pure methoxyl-free chrysophanic acid (chrysophanol) melts at 196°. Notwithstanding these differences of melting point, in the former of these papers (*loc. cit.*) it is stated that senna was the first drug in which pure chrysophanol had been observed to occur. It may therefore be noted that the three varieties of senna leaves which have now been examined were found to be devoid of chrysophanol, the only anthraquinone derivatives present being rhein and aloe-emodin.

A summary of the results of the present investigation will be found at the end of this paper.

EXPERIMENTAL.

I. Tinnevelly Senna Leaves.

The material employed for this investigation consisted of the best quality of Tinnevelly senna leaves.

A small portion (10 grams) of the ground material was treated with Prollius' fluid, and the resulting extract tested for an alkaloid with the usual reagents, but with a negative result.

Another portion (20 grams) of the ground leaves was successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—50°) extracted	0.89 gram =	4.45 per cent.
Ether	0.25 "	1.25 "
Chloroform	0.22 "	1.10 "
Ethyl acetate	1.30 "	6.50 "
Alcohol	3.18 "	15.90 "

Total = 5.84 grams = 29.20 per cent.

For the purpose of a complete examination of the constituents of the leaves, 22.54 kilograms of the dried, ground material were extracted by continuous percolation with hot alcohol. After the removal of the greater part of the solvent, 11.5 kilograms of a viscid, dark green extract were obtained.

Two kilograms of the above-mentioned extract were mixed with

water and distilled in a current of steam, when a quantity (1.5 grams) of a dark-coloured essential oil was obtained, which possessed a strong aromatic odour. There then remained in the distillation flask a dark-coloured aqueous liquid (A) and a quantity of a soft, dark green resin (B). These products were separated when cold, and the resin washed several times with aqueous ammonium sulphate, the washings being kept separate from the main bulk of the aqueous liquid. This procedure was necessitated by the fact that the resin formed an inseparable emulsion on attempting to wash it with water.

Examination of the Aqueous Liquid (A).

The aqueous liquid, after concentration under diminished pressure, was extracted many times with ether. These ethereal liquids were united, the greater part of the solvent removed, and the residue largely diluted with light petroleum (b. p. 35—50°), when the greater part of the dissolved material was precipitated as a brown solid. On decanting and concentrating the supernatant liquid, and again treating it with light petroleum, further small quantities of a similar solid were obtained, which were added to the first portion. The petroleum liquid was finally evaporated, the residue dissolved in ether, and the ethereal solution shaken successively with aqueous ammonium carbonate, sodium carbonate, and potassium hydroxide.

The ammonium carbonate extract was acidified, and extracted with ether, when a yellow, viscid product was obtained. The latter was digested with warm water and treated with animal charcoal, when the filtrate yielded a small amount of an acid, which separated in colourless needles, melting at 155°, and was identified as salicylic acid.

The sodium carbonate extract yielded only an amorphous, brown powder, but on acidifying the liquid obtained by means of aqueous potassium hydroxide a product was obtained, which was found to consist largely of aloë-emodin. This substance was subsequently obtained in larger amount, and its isolation will be described later.

Isolation of Rhein, $C_{14}H_5O_2(OH)_2 \cdot CO_2H$.

The above-mentioned brown solid which had been precipitated by means of light petroleum was digested with a considerable volume of ether, when a quantity (about 0.5 gram) of a yellowish-brown powder remained undissolved. The latter was collected, and dissolved in pyridine, from which it separated in orange-coloured needles, melting at about 318°. (Found, C=63.2; H=2.9. $C_{15}H_8O_6$ requires C=63.4; H=2.8 per cent.)

This substance is thus seen to be rhein (4:5-dihydroxyanthraquinone-2-carboxylic acid), a substance which has previously been isolated only from rhubarb. On acetylation it gave diacetylrhein, which separated from acetic anhydride in yellow needles containing solvent of crystallisation, and, after drying at 130° , melted at 258° . The apparently anomalous behaviour which had previously been observed to occur on heating diacetylrhein with xylene (T., 1911, **99**, 952) was found to be due to the loss of acetic anhydride of crystallisation.

The ethereal solution from which the crude rhein had been separated, as above described, was shaken with concentrated aqueous ammonium carbonate, when a yellowish-brown precipitate was produced. The latter was collected, and the aqueous and ethereal layers then separated, when, on acidifying the former, it yielded only a small amount of amorphous, brown material. The above-mentioned precipitate, however, proved to be the ammonium salt of rhein, which, although readily soluble in water, is practically insoluble in concentrated aqueous ammonium carbonate. It yielded rhein, melting at about $318\text{--}320^{\circ}$.

Isolation of Kaempferol, $\text{C}_{15}\text{H}_6\text{O}_2(\text{OH})_4$.

The ethereal liquid which had been extracted with aqueous ammonium carbonate, as above described, was shaken with successive portions of dilute aqueous sodium carbonate until the resulting aqueous liquids, the first of which were deep yellow, commenced to acquire a red tint. Each of the alkaline liquids was acidified as soon as it was separated from the ether, and the precipitated solid then collected. On examination, the latter proved to be a mixture of a flavone derivative with some aloe-emodin, and the complete separation of these two substances was found to be possible only by re-dissolving the mixture in ether, and repeating the above-described fractional extraction with dilute aqueous sodium carbonate two or three times, when the aloe-emodin was eventually all left behind in the ether. The flavone derivative, when freed from aloe-emodin, was crystallised by concentrating its solution in slightly diluted alcohol, when it formed small, bright yellow needles, melting at 274° , and this melting point was not altered by further crystallisation. (Found, $\text{C}=62.9$; $\text{H}=3.8$. $\text{C}_{15}\text{H}_{10}\text{O}_6$ requires $\text{C}=62.9$; $\text{H}=3.5$ per cent.)

The above-described substance, which gave a yellow colour on treatment with alkalis, and dissolved in concentrated sulphuric acid yielding a liquid possessing a strong, blue fluorescence, was identified as kaempferol (1:3:4-trihydroxyflavonol). On acetylation it yielded tetra-acetylkaempferol, which, when crystallised with

ether, ethyl acetate, or alcohol, formed colourless needles, which had a dual melting point, as observed by A. G. Perkin (T., 1902, **81**, 587); thus, fusion first occurs at about 119—120°, the product then gradually resolidifies, and subsequently melts at 183°. (Found, C=60·3; H=4·1. $C_{23}H_{18}O_{10}$ requires C=60·7; H=4·0 per cent.)

The statement made by Perkin that the dual melting point of tetra-acetylkaempferol is not due to the presence of solvent of crystallisation cannot, however, be confirmed. Specimens crystallised from each of the solvents mentioned, when carefully heated for several hours at 110°, suffered a diminution in weight without undergoing any softening, and then melted sharply at 183°; for example, an air-dried specimen which had been crystallised from ethyl acetate, on drying at 110°, gave the following results:

0·1124 lost 0·0085 of solvent. $C_4H_8O_2$ =8·6.

$C_{23}H_{18}O_{10} \cdot \frac{1}{2}C_4H_8O_2$ requires $C_4H_8O_2$ =8·8 per cent.

Tetrabenzoylkaempferol.—No benzoyl derivative of kaempferol appears heretofore to have been described. Kaempferol was benzoylated in pyridine solution, the mixture diluted with water, and the precipitated *tetrabenzoylkaempferol* collected. It was very sparingly soluble in most of the usual organic solvents, but separated in tufts of small, colourless needles when its solution in hot xylene was diluted with ethyl acetate. It had a dual melting point, similar to that of the corresponding acetyl derivative, and, in this case also, this behaviour was due to the presence of solvent of crystallisation. Tetrabenzoylkaempferol, after drying at 130°, melts at 205°, then gradually resolidifies, after which it melts at 237—238°. After drying for five hours at 170° it melts at 237—238°, without previous softening:

0·1052 * gave 0·2824 CO_2 and 0·0363 H_2O . C=73·2; H=3·8.

$C_{43}H_{26}O_{10}$ requires C=73·5; H=3·7 per cent.

No further compound could be isolated from the mother liquors from the above-described kaempferol, but in view of the statement of Tschirch and Hiepe (*Arch. Pharm.*, 1900, **238**, 439) that senna leaves contain "sennarhamnetin," it was deemed desirable further to investigate this point. An additional amount of extract was therefore worked up, and the crude flavone derivative obtained from it was submitted to the action of hydriodic acid in a Zeisel apparatus, but no methyl iodide was evolved. It is thus evident that no rhamnetin, which is a monomethyl ether of quercetin, was present in the Tinnevely senna leaves. Moreover, another sample of the same variety of leaves yielded a similar product consisting solely of kaempferol.

* Dried at 170°.

Isolation of Aloe-emodin, $C_{14}H_5O_2(OH)_2 \cdot CH_2 \cdot OH$.

The ethereal liquid from which the kaempferol had been removed, as above described, contained a substance which was somewhat slowly extracted by fairly concentrated aqueous sodium carbonate, but quickly removed by dilute potassium hydroxide. It was therefore extracted by means of the latter alkali, after which the ether was found to contain only a small amount of amorphous, neutral material. On acidifying the red, alkaline extracts, a brownish-yellow substance was precipitated, which was collected on a filter. This material was crystallised from ethyl acetate, when it yielded long, lustrous needles of a brownish-orange colour, which melted at about 218° , and proved to be aloe-emodin. (Found, $C=66.5$; $H=3.8$. Calc., $C=66.7$; $H=3.7$ per cent.) It was compared with aloe-emodin obtained from aloes and from rhubarb, and found to be identical with both these preparations. It yielded triacetylaloe-emodin, which formed pale yellow needles, melting at $174-174.5^\circ$, and tribenzoylaloe-emodin, melting at 232° . In view of the statement of Tschirch and Hiepe (*loc. cit.*, p. 435) that senna leaves contain "sennachrysophanic acid," the mother liquors from the aloe-emodin were carefully investigated for the presence of chrysophanol ("chrysophanic acid"), but with a negative result.

The aqueous liquid from which the above-described compounds had been removed by extraction with ether, as previously mentioned, was acidified with dilute sulphuric acid, when a dark-coloured, amorphous precipitate separated, and was collected. The latter consisted chiefly of resinous material, but it also contained some rhein, which had doubtless been present in the aqueous liquid in the form of a salt. The aqueous liquid, which, after this treatment, was much lighter in colour, was deprived of sulphuric acid by the cautious addition of barium hydroxide, filtered, and then extracted many times with amyl alcohol. The resulting extracts, when washed, and concentrated under diminished pressure to a small bulk, deposited, on cooling, a quantity of a brown, amorphous solid, which was collected. The filtrate from this solid yielded, on evaporation, a smaller amount of a viscid, amorphous product, but it did not appear to contain any tannin, and nothing crystalline could be directly isolated from it. A portion of it was dissolved in water, and heated with dilute sulphuric acid for some time. This resulted in the formation of some brown, resinous material, together with dextrose, but no other definite substance could be isolated. Some amorphous, glucosidic material was therefore present.

The remaining portion of the material readily soluble in cold amyl alcohol was boiled for a minute with dilute aqueous potassium hydroxide, after which it was acidified and extracted with ether. There were then obtained, in addition to brown, amorphous products, small amounts of kaempferol and aloe-emodin.

Isolation of a New Glucoside, Kaempferin, $C_{27}H_{30}O_{16}, 6H_2O$.

The material which had separated on concentrating the amyl alcohol solution, as above described, was deprived of the latter solvent, dissolved in boiling alcohol, and treated with animal charcoal, when, on cooling the filtrate, yellowish-brown, somewhat gelatinous granules separated. A little water was then added, and the mixture kept in a flask for some five months, alcohol being added from time to time to compensate for the loss by evaporation. At the end of this time yellow crystals commenced to form, and gradually spread throughout the liquid, the granular material at the same time passing into solution. The crystalline solid was then collected, and recrystallised from water, when it quickly separated in yellow needles, which melted and decomposed at $185-195^{\circ}$. This substance had the properties of a glucoside, since, when heated with dilute sulphuric acid, it yielded kaempferol (m. p. 274°) and dextrose. The latter gave *d*-phenylglucosazone, melting at 212° . No glucoside of kaempferol agreeing in properties with the one here described has previously been known, and the name *kaempferin* is therefore proposed for the new compound:

0.1741,* on heating at 155° , lost 0.0277 H_2O . $H_2O=15.8$.

0.1454 † gave 0.2804 CO_2 and 0.0655 H_2O . $C=52.8$; $H=5.0$.

$C_{27}H_{30}O_{16}, 6H_2O$ requires $H_2O=15.0$ per cent.

$C_{27}H_{30}O_{16}$ requires $C=53.1$; $H=4.9$ per cent.

0.1039 ‡ gave 0.1978 CO_2 and 0.0492 H_2O . $C=51.9$; $H=5.2$.

$C_{27}H_{30}O_{16}, H_2O$ requires $C=51.6$; $H=5.1$ per cent.

It thus appears from the above analytical results that kaempferin yields two molecules of dextrose on hydrolysis. It crystallises from water with 6 molecules of the latter, 5 of which are eliminated at 130° and the remaining one at a higher temperature. *Acetyl-* and *benzoyl-kaempferin* were prepared, but both were found to be uncrystallisable.

The original aqueous alcoholic filtrate from the crude kaempferin could not be caused to deposit any further crystalline substance, although it contained a considerable amount of material. With

* Dried in the air for fourteen hours.

† Dried at 155° .

‡ Dried until constant at 130° .

the exception of the uncrystallisable nature of the latter, its properties indicated it to be a mixture of glucosides of anthraquinone derivatives similar to that occurring in rhubarb (T., 1911, **99**, 957). It was therefore hydrolysed by heating for some time with 2·5 per cent. aqueous sulphuric acid, after which the mixture was extracted several times with ether. The resulting ethereal liquid was then examined in a manner similar to that indicated in connexion with the ether extract of the aqueous liquid, when considerable amounts of rhein and aloë-emodin were obtained, together with a little kaempferol. No chrysophanol was present. The acid aqueous liquid, from which these substances had been removed by means of ether, was deprived of sulphuric acid by treatment with barium hydroxide, when the filtered liquid was found to contain an abundance of sugar. It readily yielded *d*-phenylglucosazone, melting at 212°.

It is evident, therefore, that senna leaves contain, in addition to the new glucoside, kaempferin, a quantity of the glucosides of rhein and aloë-emodin, but, as was ascertained in connexion with the investigation of rhubarb (*loc. cit.*), these substances are devoid of purgative action.

The aqueous liquid which had been extracted with amyl alcohol was freed from the latter solvent, concentrated to a small bulk, and then largely diluted with alcohol. On keeping the mixture it deposited a considerable amount of a crystalline solid, mixed with a dark brown, syrupy product. The solid was collected, and separated so far as possible from the syrup, after which it was found possible to obtain it in a colourless condition by repeated crystallisation from dilute alcohol. This product was found to be a mixture of the sodium, potassium, and magnesium salts of an organic acid, the magnesium salt preponderating. It was fractionally crystallised many times from dilute alcohol, but no separation could be effected. No sparingly soluble salt or crystalline derivative of the acid could be prepared, nor could the acid be isolated except in the form of a gummy mass. It was impossible, therefore, to identify it.

Some of the earlier investigators have recorded the presence in senna of calcium malate and tartrate, but the above-described mixture of salts contained neither of these substances.

The original aqueous-alcoholic liquid which had been decanted from the crude mixture of salts, together with the syrupy material separated from the latter, was deprived of alcohol, diluted with water, and then treated with a slight excess of aqueous basic lead acetate. The yellow precipitate thus formed was collected, and

washed, after which it was suspended in water and decomposed by means of hydrogen sulphide. On concentrating the filtered liquid, a brown, viscid product was obtained, from which nothing crystalline could be directly separated. It was therefore boiled for a minute with dilute aqueous potassium hydroxide, acidified, and extracted with ether. There were thus obtained, in addition to dark brown, amorphous products, a little rhein, a considerable amount of kaempferol, and a moderate quantity of aloe-emodin.

The filtrate from the basic lead acetate precipitate was deprived of lead by means of hydrogen sulphide, filtered, and concentrated under diminished pressure to the consistency of a syrup. This material deposited nothing on keeping, but it evidently contained a large amount of sugar, since it readily yielded *d*-phenylglucosazone, melting at 215°.

Examination of the Resin (B).

The resin (*B*), which formed a dark green, viscid mass, amounted to about 290 grams, being thus equivalent to about 7.0 per cent. of the weight of the leaves employed. It was mixed with purified sawdust, and the dried mixture thoroughly extracted in a large Soxhlet apparatus with petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

This extract of the resin, after complete removal of the solvent, formed a dark green, oily mass, and amounted to 241 grams. It was digested with a large volume of ether, and the mixture cooled and filtered. A quantity (about 3 grams) of a green, sparingly soluble solid was thus obtained, which, after being twice distilled under diminished pressure, and crystallised several times from ethyl acetate, proved to be myricyl alcohol, a larger amount of which was subsequently isolated.

The ethereal solution from which the crude myricyl alcohol had been removed was washed with water, when a dark-coloured, aqueous liquid was obtained. The latter was found to consist of a colloidal solution of a resin, and on treatment with an aqueous solution of an inorganic salt or mineral acid it yielded a dark, resinous precipitate. Nothing definite, however, could be isolated from the latter. The washed ethereal liquid was then shaken successively with aqueous ammonium carbonate, potassium carbonate, and potassium hydroxide. Much difficulty was experienced in separating the resulting aqueous liquids owing to the formation of emulsions, which were found to be caused by the separation

of further amounts of myricyl alcohol, contaminated with much chlorophyll. The dark-coloured alkaline liquid obtained by extraction with ammonium carbonate was acidified, re-extracted with ether, and the ethereal solution fractionally extracted with aqueous ammonium carbonate. Rhein was then obtained, together with some dark-coloured, amorphous products. The alkaline liquid obtained by means of aqueous potassium carbonate, when treated in an analogous manner, yielded chiefly amorphous products, together with small amounts of kaempferol and aloe-emodin, whilst the potassium hydroxide extract yielded considerable amounts of the last-mentioned anthraquinone derivative, but no chrysophanol.

Isolation of a Phytosterolin, C₃₃H₅₆O₆.

The ethereal liquid which had been extracted with aqueous alkalis, as above described, was washed with water, when a considerable amount of dark green material was removed. The washings were acidified, and extracted with ether, and the sparingly soluble solid which had separated was then collected on a filter and washed with ether. This solid was thoroughly examined, but appeared to consist only of chlorophyll and resinous matter. The ethereal filtrate was then extracted with fairly concentrated aqueous potassium hydroxide, when small amounts of rhein and aloe-emodin were obtained. After this treatment it was washed with water, which removed a large quantity of a dark green product, whilst some neutral substance which had been occluded in the material removed by the first washing with water, described above, remained dissolved in the ether, and was added to the main bulk of the neutral constituents of the petroleum extract. The aqueous washings were acidified, and extracted with ether, when some sparingly soluble solid which separated in the form of an emulsion was collected, and well washed with ether. The solid was dried, and extracted in a Soxhlet apparatus for a long time with ethyl acetate, after which the boiling liquid was separated by filtration from some sparingly soluble solid. In this way a large amount of chlorophyll and resinous material was removed. The sparingly soluble solid separated from dilute pyridine as a black, amorphous powder, but gave a colour reaction, indicating that it contained a phytosterolin. It was therefore acetylated by heating with acetic anhydride in the presence of pyridine, when the resulting acetyl derivative crystallised from alcohol in dark-coloured leaflets. This material, after treatment with animal charcoal and repeated crystallisation from alcohol, was finally obtained in colourless, glistening leaflets, melting at 163°.

On hydrolysis with potassium hydroxide this acetyl derivative

yielded a substance which crystallised from dilute pyridine in small tufts of colourless, microscopic needles, melting at about 290° :

0.0909 gave 0.2403 CO_2 and 0.0854 H_2O . $\text{C}=72.1$; $\text{H}=10.4$.

$\text{C}_{33}\text{H}_{56}\text{O}_6$ requires $\text{C}=72.3$; $\text{H}=10.2$ per cent.

This substance was thus identified as a phytosterolin (phytosterol glucoside).

The acetyl derivative, on analysis, gave the following result:

0.1076 gave 0.2727 CO_2 and 0.0879 H_2O . $\text{C}=68.9$; $\text{H}=9.2$.

$\text{C}_{33}\text{H}_{52}\text{O}_6(\text{CO}\cdot\text{CH}_3)_4$ requires $\text{C}=68.7$; $\text{H}=8.9$ per cent.

The original ethereal filtrate from the crude phytosterolin was evaporated, and the very dark green, oily residue dissolved in methyl alcohol, and esterified by means of sulphuric acid. The mixture was then cooled, and filtered, which removed some resin and a quantity of a dark green, amorphous solid of low melting point, which could not be distilled. The methyl-alcoholic filtrate was then poured into water, the mixture extracted with ether, and the ethereal liquid deprived of a considerable amount of chlorophyll and a little unesterified acid by shaking with aqueous alkali, and subsequently washing with water. The ethereal solution was then evaporated, and the residue, which represented the crude methyl esters of the free fatty acids, purified by distillation under diminished pressure. The esters, which amounted to about 15 grams, were thus obtained as a pale brown oil, which was examined in connexion with the corresponding product from the combined acids, as described below.

Examination of the Fatty Acids.

The ethereal solutions of the neutral portion of the petroleum extract of the resin were united, and the solvent removed. The residue was then dissolved in alcohol, and hydrolysed by means of potassium hydroxide. After removing the greater part of the solvent, the mixture was poured into water, and then extracted many times with ether, for the removal of the unsaponifiable constituents. The alkaline aqueous liquid was then acidified, and extracted with ether, when a quantity of a sparingly soluble, dark-coloured solid separated in the lower portion of the ethereal layer. This solid was collected, and, when submitted to a process of purification analogous to that employed for the isolation of the previously-described phytosterolin, it yielded a further quantity of the latter. The ethereal filtrate was concentrated to a small bulk, and then largely diluted with petroleum, when a considerable amount of chlorophyll was precipitated, which was discarded. The ether-

petroleum liquid was then evaporated, and the residue dissolved in methyl alcohol, and esterified by means of sulphuric acid. On cooling the mixture a quantity of a dark green, wax-like solid separated, which was collected. This solid, on examination, was found to consist of chlorophyll, together with myricyl alcohol, which had escaped extraction during the removal of the unsaponifiable material. The methyl-alcoholic filtrate was poured into water, and the mixture extracted with ether, the resulting ethereal solution being deprived of some unesterified acid and much chlorophyll by extracting it with aqueous potassium hydroxide, and subsequently washing it with water. The ethereal liquid was then evaporated, and the residue purified by distillation under diminished pressure, when a quantity (about 15 grams) of a pale brown liquid was obtained. This portion of methyl ester, together with that previously obtained from the free fatty acids, was then fractionally distilled five times under diminished pressure, when the following fractions were obtained: Below 240° ; $240-250^{\circ}$; $250-260^{\circ}$; above $260^{\circ}/60$ mm.

The fraction boiling below 240° represented about one-third of the total material, and consisted of methyl palmitate (m. p. 29°). On hydrolysis it yielded palmitic acid, which formed colourless plates melting at 62.5° . (Found, C=74.8; H=12.5. Calc., C=75.0; H=12.5 per cent.)

The fraction boiling at $240-250^{\circ}/60$ mm. was somewhat larger than the preceding one. On hydrolysis it yielded a mixture, which contained a small proportion of unsaturated acid, but consisted for the most part of palmitic acid, together with apparently a little stearic acid.

The portion of the material distilling at $250-260^{\circ}/60$ mm., when hydrolysed, gave a small amount of unsaturated acid, together with a solid acid. The latter, when crystallised five times alternately from alcohol and ethyl acetate, yielded stearic acid melting at 69° . (Found, C=75.9; H=12.7. Calc., C=76.1; H=12.7 per cent.)

The fraction of ester boiling above $260^{\circ}/60$ mm. was too small for examination.

Examination of the Unsaponifiable Material.

The combined ethereal extracts containing the unsaponifiable material, which had been obtained as above described, were washed, dried, and evaporated. The residue was then heated with a large amount of alcohol, and the mixture filtered whilst hot, thereby removing a quantity of almost black, tarry material. The filtrate, which was dark brown, deposited, on cooling, a quantity of an

indistinctly crystalline solid, which was collected, and again crystallised from alcohol. This was then crystallised once from ethyl acetate, and distilled under diminished pressure, when it passed over at a high temperature as an almost colourless liquid, which solidified on cooling. The distillate was then crystallised twice from ethyl acetate, with the employment of animal charcoal, when a quantity (about 8 grams) of small, colourless leaflets, melting at 83° , was obtained. (Found, $C=82.1$; $H=14.5$. $C_{30}H_{62}O$ requires $C=82.2$; $H=14.5$ per cent.)

This substance was therefore myricyl alcohol.

Isolation of a Phytosterol, $C_{27}H_{46}O$.

The combined alcoholic mother liquors from the crude myricyl alcohol were diluted somewhat with water, and kept for some time, when a quantity of crystalline material, together with much orange-red-coloured oil, was deposited. The solid was collected, when it was found to be a mixture of myricyl alcohol, and a substance which appeared to be a phytosterol. The myricyl alcohol was eliminated by fractional crystallisation from warm ethyl acetate, in which it was more sparingly soluble than the phytosterol. A product was then finally obtained, which, when crystallised from a mixture of ethyl acetate and dilute alcohol, formed large, lustrous plates, melting at $142-143^{\circ}$:

0.2932, on heating at 130° , lost $0.0162 H_2O$. $H_2O=5.5$.

0.0986 * gave $0.2967 CO_2$ and $0.1033 H_2O$. $C=83.6$; $H=11.9$.

$C_{27}H_{46}O, H_2O$ requires $H_2O=4.5$ per cent.

$C_{27}H_{46}O$ requires $C=83.9$; $H=11.9$ per cent.

The optical rotation of the phytosterol was determined, with the following result:

0.2770,* made up to 20 c.c. with chloroform, gave $\alpha_D -1.03'$ in a 2-dm. tube, whence $[\alpha]_D -37.8^{\circ}$.

This phytosterol yielded an acetyl derivative, which formed pearly leaflets, melting at 128° .

The filtrate from the crude phytosterol, which contained the greater part of the unsaponifiable material, was carefully examined, but only orange-coloured, oily products could be obtained from it.

Ether, Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

The ether extract of the resin was a dark, brownish-green mass, and amounted to 14.4 grams. On examination it was found to contain, in addition to chlorophyll, some fatty matter, myricyl

* Dried at 130° .

alcohol, and a considerable proportion of rhein and aloë-emodin, but no kaempferol was present.

The chloroform extract of the resin amounted to only 3 grams, and consisted of a dark greenish-brown resin.

The ethyl acetate extract amounted to 2 grams, and was similar in character to the last-mentioned extract.

The alcohol extract was a dark brown resin, amounting to 20 grams, and nothing definite could be obtained from it.

II. *Senna Leaves from Peru.*

This material consisted of a sample of senna leaves which had been obtained from Lima, Peru, and concerning which the following information was supplied: "During the last few years there has been introduced into England, from Port Royal (Jamaica), and recently from the interior of Peru, a new species of senna (*Cassia lanceolata*, var. *Porturegalis*), the characters of which are as follows: The flavour of its infusion, which is clear, and nearly colourless, much resembles that of tea. It is very purgative, and at the same time it is not nauseous, nor does it cause griping or irritation. On account of these properties it is much valued for the debilitated, the aged, women, and children."

A sample of these leaves, together with buds, flowers, and pods, was submitted to Mr. E. M. Holmes, F.L.S., who kindly compared them with specimens at Kew and at the British Museum, when they were found to be, botanically, quite identical with well-developed specimens of Tinnevely senna (*Cassia angustifolia*, Vahl). As is shown below, they differed somewhat from the Tinnevely senna leaves, the examination of which has just been described, both in the amount of resin, the proportions of the various extracts, and in some of their constituents. The differences observed, however, are only such as might be accounted for by the altered conditions of climate and soil.

As a preliminary experiment, a portion (20 grams) of the ground leaves was extracted successively in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—50°) extracted	0.82 gram	=	4.10 per cent.
Ether	0.70 "		3.50 "
Chloroform	0.26 "		1.30 "
Ethyl acetate	0.47 "		2.35 "
Alcohol	2.25 "		11.25 "

Total = 4.50 grams = 22.50 per cent.

A quantity (3.365 kilograms) of the ground leaves was then thoroughly extracted in a large Soxhlet apparatus with boiling

alcohol, after which the resulting extract was concentrated, and examined in a manner analogous to that described in connexion with the investigation of the Tinnevely leaves.

A small amount of essential oil was removed by means of steam, after which the resin was separated from the water-soluble constituents. The aqueous liquid was extracted first with ether, and subsequently with amyl alcohol, after which it was found to contain considerable sugar, together with amorphous products, which yielded kaempferol on hydrolysis.

The ethereal extract, on examination, yielded, in addition to some amorphous products, aloë-emodin, rhein, and a product having the properties of a flavone derivative. The latter was, however, in part, much more sparingly soluble in alcohol than the corresponding material from the Tinnevely leaves. The portion which was sparingly soluble crystallised from alcohol in small, yellow needles, melting at 302° . (Found, C=60.9; H=4.1. $C_{16}H_{12}O_7$ requires C=61.2; H=3.8 per cent.)

This substance was found to be identical with *isorhamnetin*, which was first isolated by A. G. Perkin (T., 1896, **69**, 1658) from the flowers of the yellow wallflower, and subsequently by Power and Salway from red clover flowers (T., 1910, **97**, 245). The melting point observed in the present instance is, however, a little higher than that previously recorded. The substance yielded tetra-acetyl-*isorhamnetin*, which formed thin, colourless needles, melting at 201° .

The alcoholic mother liquors from the *isorhamnetin* gave a product which, when acetylated, yielded tetra-acetylkaempferol, identical with that obtained from the Tinnevely leaves. It crystallised from alcohol with half a molecule of solvent of crystallisation:

0.1421 ,* on heating at 130° , lost $0.0062 C_2H_6O$. $C_2H_6O=4.6$.

$C_{23}H_{18}O_{10} \cdot \frac{1}{2} C_2H_6O$ requires $C_2H_6O=4.8$ per cent.

The amyl alcohol extract of the aqueous liquid yielded some viscid, brown material, which was readily soluble in amyl alcohol, and a yellow, amorphous product, sparingly soluble in dry amyl alcohol. The viscid material, on treatment with alkali, yielded *isorhamnetin* and kaempferol, the latter preponderating, whilst the sparingly soluble, yellow product was found to be a mixture of glucosides. It would not crystallise, and no individual substance could be separated from it. On hydrolysis with dilute aqueous sulphuric acid it yielded dextrose, rhein, *isorhamnetin*, kaempferol, and aloë-emodin.

* Air-dried substance.

Examination of the Resin.

The resin was a soft, dark green mass, and amounted to 196 grams, being thus equivalent to 5·8 per cent. of the weight of the leaves employed.

The petroleum extract, which amounted to 137 grams, yielded, in addition to chlorophyll and amorphous products, the following definite substances: Myricyl alcohol (m. p. 83°); a phytosterol, $C_{27}H_{46}O$ (m. p. 142—143°); a phytosterolin, $C_{33}H_{56}O_6$; rhein; aloë-emodin; palmitic and stearic acids, and a small amount of unsaturated acid. Chrysophanol was absent.

The ether extract amounted to 18·5 grams. It consisted chiefly of resinous material and chlorophyll, but also yielded small amounts of rhein, aloë-emodin, and the above-mentioned mixture of flavone derivatives.

The chloroform, ethyl acetate, and alcohol extracts of the resin amounted to 9, 7, and 24 grams respectively. They all consisted of black, amorphous masses, and nothing definite could be isolated from any of them.

III. Alexandrian Senna Leaves.

In order to make the present investigation complete, it was deemed desirable also to make an examination of Alexandrian senna leaves, especially on account of the fact that Tschirch and Hiepe (*loc. cit.*) have stated that senna leaves contain "senna-emodin," which was considered to be identical with aloë-emodin, "senna-isoemodin," "sennarhamnetin," and "sennachrysophanic acid" (chrysophanol). In the present case no attempt was made to conduct a complete examination of the leaves, attention being chiefly directed to the examination of the anthraquinone and flavone derivatives, and their glucosides.

Ten pounds of a good quality of Alexandrian senna leaves were ground, and extracted in a large Soxhlet apparatus, first with ether, and then with alcohol, the resulting extracts being subsequently examined in the direction indicated, with the employment of methods similar to those already described. It was then found that the anthraquinone derivatives present consisted solely of rhein and aloë-emodin, whilst the flavone derivatives were *isorhamnetin* and *kaempferol*, the former preponderating. These four substances were also found to be present in the form of glucosides, and in much greater proportion as such than in the free state. Myricyl alcohol and a phytosterolin were also isolated.

Summary.

The results of the present investigations may be summarised as follows:

The material employed consisted of (I) Tinnevelly senna leaves (*Cassia angustifolia*, Vahl); (II) senna leaves from Lima, Peru, which were found to be botanically identical with the Tinnevelly leaves; (III) Alexandrian senna leaves. The last-mentioned species is usually recognised as *Cassia acutifolia*, Delile, but by some authorities it is regarded simply as a variety of *Cassia angustifolia*.

(I) An alcoholic extract of the Tinnevelly leaves, when distilled with steam, yielded a small amount of an essential oil. From the portion of the extract which was soluble in water the following substances were isolated: (i) Salicylic acid, (ii) rhein, $C_{15}H_8O_6$; (iii) kaempferol, $C_{15}H_{10}O_6$; (iv) aloë-emodin, $C_{15}H_{10}O_5$; (v) *kaempferin*, $C_{27}H_{30}O_{16} \cdot 6H_2O$ (m. p. 185—195°), a new glucoside of kaempferol; (vi) a mixture of the glucosides of rhein and aloë-emodin; (vii) the magnesium salt of an unidentified organic acid. The aqueous liquid furthermore contained a quantity of a sugar which yielded *d*-phenylglucosazone (m. p. 216°), and some brown, amorphous products, which, on treatment with alkali, gave kaempferol, together with small amounts of rhein and aloë-emodin. Some amorphous, glucosidic material was also present.

The portion of the alcoholic extract which was insoluble in water consisted of a soft, dark green resin, which amounted to 7.0 per cent. of the weight of the leaves employed. From this material, which contained considerable chlorophyll and amorphous products, there were isolated, in addition to some of the substances mentioned above, the following compounds: (i) Myricyl alcohol; (ii) a phytosterol, $C_{27}H_{46}O$; (iii) a phytosterolin, $C_{33}H_{56}O_6$; (iv) palmitic and stearic acids.

(II) The senna leaves from Lima, Peru, were found to contain all the above-mentioned compounds, with the exception of the magnesium salt, and, in addition, *isorhamnetin*. A glucoside of *isorhamnetin* was also present in association with glucosides of kaempferol, rhein, and aloë-emodin, but no pure compound could be isolated from the mixture.

(III) Alexandrian senna leaves yielded, in addition to myricyl alcohol and a phytosterolin, rhein, aloë-emodin, kaempferol, and *isorhamnetin*. These four substances were also present in the form of glucosides, and in much greater proportion as such than in the free state.

The statements of Tschirch and Hiepe (*Arch. Pharm.*, 1900, 238, 427) that senna leaves contain "sennaisoemodin," "senna-

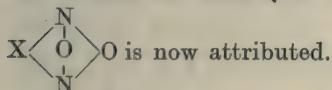
chrysophanic acid" (chrysophanol), and a "substance, $C_{14}H_{10}O_5$," could not be confirmed, it having been ascertained that the anthraquinone derivatives present consist solely of rhein and aloë-emodin. In this connexion it may be noted that a mixture of approximately equal quantities of the last-mentioned two compounds has the empirical composition and properties assigned by Tschirch and Hiepe to the "substance, $C_{14}H_{10}O_5$." Furthermore, the "sennarhamnetin" of the last-mentioned authors has been found to be identical with the *isorhamnetin* previously described by Perkin (T., 1896, **69**, 1658).

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CCXIV.—*The Conversion of Orthonitroamines into isoOxadiazole Oxides (Furoxans).*

By ARTHUR GEORGE GREEN and FREDERICK MAURICE ROWE.

IN the two previous communications (T., 1912, **101**, 2452; this vol., p. 897) it has been shown that many *o*-nitroamines on oxidation by means of sodium hypochlorite in alkaline solution are converted into furoxans (furazan oxides), to which the constitution



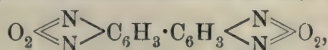
In order to investigate the limits of this reaction and the extent to which it is influenced by substitution of hydrogen in the para-position, we have now studied the action of alkaline sodium hypochlorite on the following compounds: 2:4-Dinitroaniline, nitro-*p*-phenylenediamine, 2-nitro-4-acetyl-*p*-phenylenediamine, 3-nitro-4-aminobenzeneazo- β -naphthol, *o*-nitroaniline-*p*-sulphonic acid, and *o*-dinitrobenzidine. These compounds may be regarded as derivatives of *o*-nitroaniline, in which the para-hydrogen atom is replaced by the nitro-, amino-, acetylamino-, azonaphthol, sulphonic, and phenyl groups respectively. It has already been shown in the case of dinitroaniline that when the oxidation is effected in methyl- or ethyl-alcoholic solution the formation of the furoxan is accompanied by a remarkable replacement of the *p*-nitro-group by methoxyl or ethoxyl, a fact which confirms the hypothesis that the reaction is a quinonoid one, recalling the ready replacement of

electronegative groups in the quinonoid nucleus, as, for example, of the sulphonic group in β -naphthaquinonesulphonic acid. A variety of experiments, which have since been performed, have demonstrated that the *p*-nitro-group in dinitroaniline cannot in any circumstances be preserved intact. When the oxidation is effected in absence of an alcohol by employing a fine aqueous suspension of the base in place of an alcoholic solution, no product at all could be isolated, and judging from the large amount of chloropicrin produced, the benzene nucleus was completely destroyed. A similar result was obtained on submitting to oxidation with sodium hypochlorite aqueous solutions of nitro-*p*-phenylenediamine, nitroacetyl-*p*-phenylenediamine, and the azo-compound obtained by combining diazotised nitro-*p*-phenylenediamine with β -naphthol. In all these instances oxidation took place readily, but apparently with complete disruption of the ring, since a strong odour of chloropicrin was always observed, and nothing could be isolated from the solution. This was the case whether the oxidation was effected at 15° or at 0°, and whether in an alcoholic or in aqueous solution. Very much the same result was obtained by the oxidation of *o*-nitroaniline-*p*-sulphonic acid, although in this instance it was found possible to isolate a small quantity of a compound which appeared to be the furoxansulphonic acid, $\text{SO}_3\text{H} \cdot \text{C}_6\text{H}_3 \cdot \text{N}_2\text{O}_2$. The greater part of the product, however, suffered complete destruction, and much sodium sulphate was obtained. It might have been anticipated that *o*-nitroaniline-sulphonic acid would have behaved on oxidation in an alcoholic solution similarly to dinitroaniline, an alkyloxy-group taking the place of the sulphonic group, but no trace of such a product could be detected.

It appears, therefore, that the amino-, acetylamino-, azo-, and sulphonic groups (and in aqueous solution also the nitro-group), when occupying the para-position with respect to the amino-group in a substituted *o*-nitroaniline, render the benzene ring unstable to hypochlorite oxidation. On the other hand, we have previously shown that the stability of the ring is not diminished by the presence of a chlorine atom or methyl group.

The oxidation of *o*-dinitrobenzidine appeared to offer considerable interest both from the above point of view and also on account of the apparent existence of this base in two isomeric forms, as recently pointed out by Cain, Coulthard, and Micklethwait (T., 1912, 101, 2298). We have therefore submitted the two isomerides under like conditions of reaction to the hypochlorite oxidation, and have obtained the following remarkable result. The dinitrobenz-

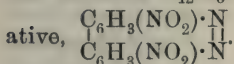
idine melting at 275°, which Cain regards as a 3:5'-form, produces a typical furoxan (bisbenzisooxadiazole oxide),



which is a pale yellow substance, readily convertible into a diphenoquinonetetraoxime, $\text{C}_6\text{H}_3(\text{:NOH})_2 \cdot \text{C}_6\text{H}_3(\text{:NOH})_2$, and a bis-

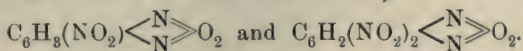
benzisooxadiazole, $\text{O} \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C}_6\text{H}_3 \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{N} \\ \diagdown \quad \diagup \\ \text{N} \end{array} \text{O}$. On the other hand,

the isomeride melting at 233°, regarded by Cain as the 3:3'-form, gives no furoxan, but a reddish-orange, crystalline compound of the formula $\text{C}_{12}\text{H}_6\text{O}_4\text{N}_4$, which is probably an internal azo-derivative,



Neither of the hypotheses hitherto advanced to account for this interesting form of isomerism would seem adequate to give an explanation of this result. Especially untenable is the view of Cain, Macbeth, and Stewart (this vol., p. 586), based on the absorption spectra of the two isomerides, for even if the two constitutions suggested were not interconvertible, which is difficult to believe possible, the hemi-quinonoid arrangement should give at least a monofuroxan. It seems possible that an explanation might be based on the formula for benzidine with superimposed nuclei suggested by Kaufler (*Ber.*, 1907, **40**, 3250), but the matter requires further investigation.

Finally we have submitted to re-examination the so-called "nitro-*o*-dinitrosobenzene," $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{N}_2\text{O}_2$, and "dinitro-*o*-dinitrosobenzene," $\text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{N}_2\text{O}_2$, obtained by Drost (*Annalen*, 1899, **307**, 54) by nitration of benzisooxadiazole (then termed *o*-dinitrosobenzene). The fact that the latter of these compounds is stated to give rise to salts of the type $\text{C}_6\text{H}(\text{NO}_2)_2\text{N}_2\text{O}_2\text{M}'$ seemed to call in question the correctness of the constitution assigned, and to render reinvestigation desirable. The two compounds were readily obtained by nitration of the benzisooxadiazole (benzfuroxan) prepared by hypochlorite oxidation of *o*-nitroaniline. As thus prepared, they exhibited all the properties ascribed to them by Drost, and gave on analysis numbers corresponding with the mono- and di-nitro-derivatives of benzisooxadiazole,



Both compounds were found to possess somewhat strongly-developed acid properties, rendering Congo paper blue and decomposing carbonates. By treatment with potassium hydrogen carbonate, the dinitro-compound was converted into the yellow, crystalline

potassium salt described by Drost. This gave on analysis numbers corresponding with the empirical formula $C_6HK(NO_2)_2 \cdot N_2O_2$, and on treatment with dilute sulphuric acid was reconverted into the parent compound, of which it is therefore a true salt. A corresponding salt could not be isolated from the mononitro-derivative, although this dissolves readily in alkalis, and also gives a reddish-brown precipitate on adding sodium ethoxide to its benzene solution. Both the mono- and the di-nitro-compounds readily suffer destructive decomposition by dilute alkalis, especially alkali hydroxide, in which they dissolve freely, giving deep red solutions and producing nitrites and ammonia. For this reason all attempts to convert them into the corresponding nitro-*o*-dioximes proved unsuccessful. The failure to obtain the latter compounds affords, however, no sufficient ground for doubting the correctness of the formulæ assigned, and we seem to have here a case in which strong acidic properties are evidenced by hydrogen in the benzene ring.

EXPERIMENTAL.

o-Dinitrobenzidines.

The two isomeric *o*-dinitrobenzidines were prepared as described by Brunner and Witt (*Ber.*, 1887, **20**, 1023) and by Bandrowski (*Ber.*, 1884, **17**, 1181) respectively. It was found that the two compounds could be readily separated from each other, and quickly obtained in a pure state by making use of the large difference in basicity which exists between them. Whilst the isomeride melting at 275° , which is obtained by the nitration of diacetylbenzidine, is entirely precipitated as free base when its solution in nearly concentrated hydrochloric acid is diluted with water (thus closely resembling *o*-nitroaniline), a similar solution of the isomeride melting at 233° , obtained by the nitration of diphtalylbenzidine, is not basified on dilution, and requires to be precipitated by alkali. The two bases possessed the appearance and melting points assigned to them by Cain, Coulthard, and Micklethwait.

Bisbenzisooxadiazole Oxide (Bisbenzfuroxan or Bisbenzfurazan Oxide),

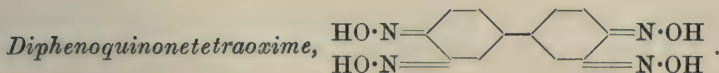


o-Dinitrobenzidine (m. p. 275°), converted into a finely-divided precipitate by solution in concentrated sulphuric acid, dilution with water, and washing free from acid, was made into a paste with sodium hydroxide solution (40 per cent. NaOH), and treated with

an excess of sodium hypochlorite (10 per cent. active chlorine). The mixture was then slowly heated to the boiling point. At a temperature of about 95° the suspended dinitrobenzidine changed in colour from a deep red to a pale buff-yellow. The mixture was boiled until no further lightening of tint took place, and the precipitate was then collected and washed with water. If it still contains any unaltered dinitrobenzidine, this can be removed by extraction with boiling concentrated hydrochloric acid. The product is a pale yellow precipitate, insoluble in water, very sparingly soluble in alcohol, more readily so in acetone, and easily soluble in hot pyridine, tetrachloroethane, or chlorobenzene. The latter is the best medium for crystallisation, and from it the compound was obtained in thin, yellow, hexagonal plates, melting at 211° . It is not volatile with steam, and dissolves in concentrated sulphuric acid to a yellow solution, from which it is reprecipitated by water:

0.0654 gave 11.95 c.c. N_2 at 25° and 751 mm. $N=20.84$.

$C_{12}H_6O_4N_4$ requires $N=20.74$ per cent.



Four grams of the pure bisbenzisooxadiazole oxide were dissolved in concentrated sulphuric acid and poured into water. The finely-divided product was collected, washed free from acid, and suspended in water. Six grams of hydroxylamine hydrochloride were then added, and after warming to about 50° , aqueous sodium hydroxide was run in until complete solution occurred. Care must be taken that the temperature does not rise too high, as the dioxime is rapidly converted into the bisbenzisooxadiazole at temperatures above 60° . The blood-red solution after filtration was acidified with acetic acid, when the dioxime separated as a colloidal precipitate, which it was not found possible to crystallise. When dry it forms a brown, amorphous powder, melting at 235° , very sparingly soluble in organic solvents, but dissolving readily in alkalis or concentrated acids, giving red solutions. It has weak mordant-dyeing properties. On oxidation with sodium hypochlorite it is reconverted into bisbenzisooxadiazole oxide, and on heating with alkalis into bisbenzisooxadiazole:

0.0582 gave 10.45 c.c. N_2 at 22° and 748 mm. $N=20.61$.

$C_{12}H_{10}O_4N_4$ requires $N=20.44$ per cent.

Bisbenzisooxadiazole (Bisbenzfurazan),

The caustic alkaline solution of the bisdioxime was heated until it was nearly colourless. The precipitated bisbenzisooxadiazole was collected, washed, dried, and recrystallised from glacial acetic acid, and then from chlorobenzene. It forms yellow needles, which melt at 244° . It dissolves in concentrated sulphuric acid with a yellow colour, and is precipitated unchanged as a nearly colourless precipitate on addition of water:

0.0728 gave 15.1 c.c. N_2 at 25° and 751 mm. $N=23.67$.

$C_{12}H_6O_2N_4$ requires $N=23.53$ per cent.

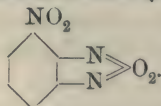
Oxidation of Dinitrobenzidine of m. p. 233° .

The oxidation with hypochlorite was effected in exactly the same manner as in the case of the other isomeride, but took place with considerably greater difficulty. Instead of becoming paler, the precipitate assumes a darker tint. The product was collected, washed with water, extracted with hydrochloric acid to remove unaltered dinitrobenzidine, and the residue was crystallised from chlorobenzene. The product was thus obtained in bunches of small, reddish-orange needles, which darken at 200° and melt at 220° :

0.0804 gave 14.4 c.c. N_2 at 25° and 766 mm. $N=20.84$.

$C_{12}H_6O_4N_4$ requires $N=20.74$ per cent.

The substance did not behave like a furoxan, and could not be converted by reduction with alkaline hydroxylamine into a dioxime. It dissolves with a red colour in concentrated sulphuric acid.

6-Nitrobenzisooxadiazole Oxide (6-Nitrobenzfuroxan),

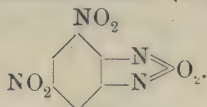
Benzisooxadiazole oxide, dissolved in concentrated sulphuric acid, was nitrated in the cold with one molecular proportion of nitric acid (D 1.52), mixed with an equal volume of concentrated sulphuric acid. The product, when crystallised from acetic acid, formed thin, yellowish-brown plates, melting at 143° . It had marked acidic properties:

0.0681 gave 13.7 c.c. N_2 at 19° and 750 mm. $N=23.40$.

$C_6H_3O_4N_3$ requires $N=23.20$ per cent.

The alcoholic solution on addition of sodium sulphide gives a deep blue coloration, soon passing into violet and brown.

4:6-Dinitrobenzisooxadiazone Oxide (4:6-Dinitrobenzfuroxan),



Ten grams of benzisooxadiazone oxide, dissolved in 120—150 c.c. of concentrated sulphuric acid, were nitrated by addition of a mixture of 15 c.c. of nitric acid (D 1.52) and 40 c.c. of concentrated sulphuric acid. The mixture is cooled at first, and then warmed to 40° and poured into water. The product, when crystallised from acetic acid, forms large, yellow needles, melting at 172°. It has pronounced acid properties, turning Congo paper blue, and dissolving easily in aqueous alkali. The alkaline solutions readily undergo decomposition, with formation of ammonia and nitrites:

0.1292 gave 27.7 c.c. N_2 at 19° and 750 mm. $N = 24.93$.

$C_6H_2O_6N_4$ requires $N = 24.78$ per cent.

The potassium salt, prepared as described by Dröb, was obtained in yellowish-brown, glistening plates soluble in water.

DEPARTMENT OF TINCTORIAL CHEMISTRY,
THE UNIVERSITY, LEEDS.

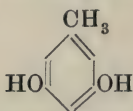
CCXV.—*Substituted Dihydroresorcins. 1-Methyldihydroresorcin and 2-Methyldihydroresorcin.*

By CHARLES GILLING.

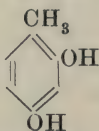
IN the preparation of hydroaromatic compounds from aromatic hydroxy-acids it has been observed that only those compounds which contain the hydroxyl and carboxyl groups in the meta-position to one another are susceptible of reduction in the desired way (compare Baudisch, Hibbert, and Perkin, T., 1909, **95**, 1870).

It seemed, therefore, to be of interest to ascertain whether a similar rule holds good for the reduction of the dihydroxytoluenes. Unfortunately, most of these compounds are difficult to prepare in quantity, and as the author has found it impracticable to continue the research for the present, it seems desirable to give a brief account of the experiments on the reduction products of orcinol (I) and of cresorcinol (II) so far as they were completed when working in the research laboratory of the Pharmaceutical Society in 1911.

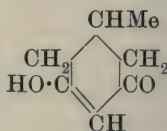
Orcinol was first reduced by Vorländer (*Ber.*, 1897, **30**, 1801), using sodium amalgam, the reduction product being 1-methyldihydroresorcin (III). This compound was also prepared by the same author by condensing ethyl crotonate with ethyl acetoacetate and hydrolysing the resulting ester (*Annalen*, 1899, **308**, 195):



(I.)

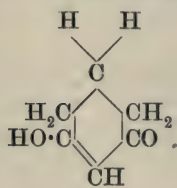


(II.)

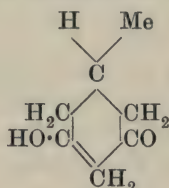


(III.)

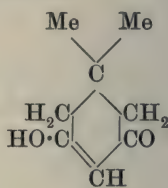
Several new derivatives of this substance are now described, the most interesting of which are those produced by its esterification. Methyldihydroresorcin is the intermediate member of the series, which comprises dihydroresorcin (IV) and dimethyldihydroresorcin (V), but, unlike either, its molecule is unsymmetrical:



(IV.)

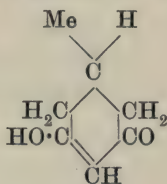


(III.)



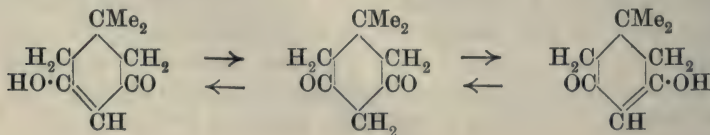
(V.)

It would therefore appear that a second form of this substance having the configuration VI should be capable of existence:



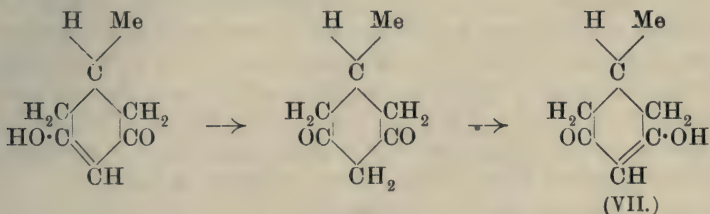
(VI.)

Much evidence has been brought forward to show that dihydro- and dimethyldihydro-resorcins are tautomeric substances; thus they yield monobasic silver salts and dioximes, and from spectroscopic observations it is probable that their molecules, in solution at least, are continually changing from one form to another, as represented in the following scheme:



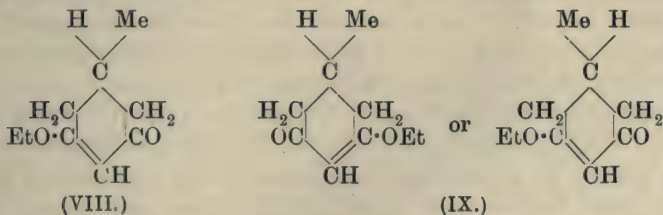
The introduction of an ethyl group in place of the mobile hydrogen atom destroys this tautomerism.

Assuming that 1-methyldihydroresorcin behaves in a similar way, the change will be represented:



and it will be seen that the configuration (VII) is identical with that denoted by (VI), and it follows that 1-methyldihydroresorcin will exist in only one form, a form, however, in which a tautomeric change is continually taking place. This view is in agreement with the observed facts, for although a careful search has been made among the reaction products for a second modification, none was ever found.

When 1-methyldihydroresorcin is esterified with ethyl alcohol and sulphuric acid, the product is a liquid from which crystals can be separated by freezing. Both crystals and mother liquor give similar figures on analysis, except that the former contain a molecule of water of crystallisation, and it seems, therefore, most probable that two ethyl ethers are formed, the ethyl group sometimes entering the molecule in the phase represented by (III) and sometimes in the phase (VII), giving rise to the two compounds (VIII) and (IX), which stand in the relationship of *cis*- and *trans*-forms to one another:



The author intends to investigate more fully than has been done up to the present the preparation of 2-methyldihydroresorcin, since this substance, if the above considerations hold good, should yield four isomeric ethyl ethers.

EXPERIMENTAL.

Preparation of 1-Methyldihydroresorcin.

This substance was prepared according to the directions of Vorländer, but it was found that after repeatedly crystallising the crude substance from ethyl acetate it melted at 127° (Vorländer gives 122°) with the formation of a red film on the side of the capillary.

The *silver* salt, prepared in the usual manner, is a lemon-yellow substance, which slowly darkens on exposure to light:

0.2012 gave 0.0927 Ag. $\text{Ag}=46.07$.

$\text{C}_7\text{H}_9\text{O}_2\text{Ag}$ requires $\text{Ag}=46.30$ per cent.

The *disemicarbazone*, prepared by adding the alcoholic solution to a solution of semicarbazide acetate, is a white, amorphous substance, insoluble in all the ordinary solvents. It darkens when heated to 215° , and decomposes at 225° . For analysis it was well washed with alcohol and dried:

0.1037 gave 31.2 c.c. N_2 at 17° and 754 mm. $\text{N}=34.62$.

$\text{C}_9\text{H}_{16}\text{O}_2\text{N}_6$ requires $\text{N}=35.0$ per cent.

Esterification of 1-Methyldihydroresorcin.

Twenty grams were boiled with 100 c.c. of absolute alcohol and 7.5 grams of sulphuric acid under reflux on the water-bath for six hours. The liquid was poured into water, extracted four times with ether, the ethereal solution washed with dilute sodium hydroxide, then with water, and dried, evaporated, and the residue immediately distilled, when 12.5 grams passed over at $147\text{--}152^{\circ}/36$ mm. After two more distillations, the product, which was evidently a mixture of two stereoisomeric modifications of the ethyl ether of 1-methyldihydroresorcin, was analysed:

0.1185 gave 0.3030 CO_2 and 0.0940 H_2O . $\text{C}=69.73$; $\text{H}=8.81$.

$\text{C}_9\text{H}_{14}\text{O}_2$ requires $\text{C}=70.13$; $\text{H}=9.09$ per cent.

On cooling in a freezing mixture and freely exposing to air, a partial solidification took place, and the whole was spread on a porous plate (A), when 6 grams of a solid were obtained. This was crystallised from well-cooled diluted acetone:

0.1023 gave 0.2360 CO_2 and 0.0859 H_2O . $\text{C}=62.91$; $\text{H}=9.33$.

$\text{C}_9\text{H}_{14}\text{O}_2, \text{H}_2\text{O}$ requires $\text{C}=62.79$; $\text{H}=9.30$.

3-Ethoxy-1-methyl- Δ^3 -cyclohexen-5-one (form a) is freely soluble in all the ordinary solvents, but may be crystallised from cold dilute acetone, from which it separates in fine, feathery needles melting at 42° . It has a peculiar, fragrant, and camphoraceous

odour. When placed in a vacuum desiccator it first loses water of crystallisation and liquefies, and afterwards slowly volatilises:

0.6907 lost in six hours 0.0759. $H_2O = 10.09$.

$C_9H_{14}O_2, H_2O$ requires $H_2O = 10.5$ per cent.

The residue then suffered a further loss of 0.01 gram per twenty-four hours. The anhydrous substance is a colourless, oily liquid.

The porous plate (A), after removal of the above, was extracted with ether, when, after removing the solvent, 5 grams of an oil were obtained. No further quantity of the above-described crystalline ester could be obtained from this by cooling, adding water, or exposing to a moist atmosphere in a closed vessel for several days, and it is doubtless the second modification of the ethyl ether, although possibly not entirely free from the first form. On remaining for a long time exposed to the air, it deposited crystals which melted at 125° with a red film, nor was this melting point altered by admixture with pure 1-methyldihydroresorcin. This hydrolysis can be more rapidly effected by heating either modification for half-an-hour on the water-bath with an alcoholic solution of sodium hydroxide.

The two ethers were also prepared by heating the silver salt of 1-methyldihydroresorcin suspended in dry benzene with the theoretical amount of ethyl iodide. After removing the silver iodide and evaporating, an oily liquid remained, which partly solidified when cooled in a freezing mixture. The solid, after crystallising from dilute acetone, melted at 42° , and its identity was confirmed by the mixed melting-point method.

Reduction of Cresorcinol.

Cresorcinol (2:4-dihydroxytoluene) was prepared from *o*-toluidine according to the directions of Noeltig (*Ber.*, 1884, **17**, 265) and Michael and Grandmougin (*Ber.*, 1893, **26**, 2349). Seventeen grams were boiled with 17 grams of sodium hydrogen carbonate, 100 c.c. of water, and 1000 grams of 2 per cent. sodium amalgam for fifteen hours under reflux in a stream of carbon dioxide. The aqueous liquid was then poured off, a further 20 grams of sodium hydrogen carbonate added, and the whole extracted twice with ether to remove unchanged material. Excess of dilute sulphuric acid was then run in, and the liquid extracted five times with chloroform, the chloroform solution dried over sodium sulphate and evaporated, when a sticky syrup remained. After several weeks a small amount of solid (m. p. $66-70^\circ$) separated, but as it was only obtained in very small amount, and as it proved very difficult to crystallise, the crude material was used for the preparation of the following derivative.

2-Methyldihydroresorcinanilide was prepared by dissolving 2 grams of the oil with 1.5 grams of aniline in 20 c.c. of dry benzene, and boiling under reflux for ten hours. On adding a few drops of light petroleum a solid separated, which was crystallised from ethyl acetate:

0.3302 gave 19.4 c.c. N_2 at 14° and 762 mm. $N=6.93$.

$C_{13}H_{15}ON$ requires $N=6.96$ per cent.

This substance is insoluble in light petroleum, readily soluble in chloroform, and can be crystallised from benzene or ethyl acetate, from which it separates in rosettes of yellowish-sandy needles melting at 162° .

The disemicarbazone was prepared by dissolving 1 gram of the crude 2-methyldihydroresorcin in alcohol, and adding a solution of semicarbazide acetate, when a pinkish-white, amorphous substance slowly separated. This was washed with alcohol, and dried:

0.1090 gave 33 c.c. N_2 at 20° and 755 mm. $N=34.63$.

$C_9H_{16}O_2N_6$ requires $N=35.0$ per cent.

The disemicarbazone is insoluble in all the ordinary solvents, and, when heated, darkens at 220° , and melts and decomposes at $224-225^\circ$.

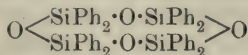
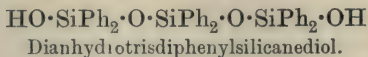
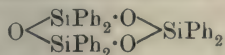
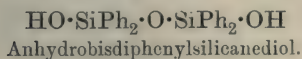
The author wishes to express his thanks to the Research Fund Committee of the Chemical Society for a grant which has in part defrayed the expenses of this investigation.

CCXVI.—A Study of Some Organic Derivatives of Tin as Regards their Relation to the Corresponding Silicon Compounds. Part II. Condensation Products of Dihydroxydibenzylstannane.

By THOMAS ALFRED SMITH and FREDERIC STANLEY KIPPING.

It has been shown recently (Kipping, T., 1912, **101**, 2108; Robison and Kipping, *loc. cit.*, p. 2142) that the dihydroxy-compounds of the molecular formula $SiR_2(OH)_2$ are, as a rule, stable at the ordinary temperature, but that in the presence of relatively small proportions of alkalis or acids they readily undergo condensation, giving open-chain and closed-chain products; diphenylsilicanediol,

for example, gives the following series of compounds (as well as others not yet described):



Trianhydrotetradiphenylsilicanediol. Tetra-anhydrotetradiphenylsilicanediol.

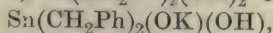
Now derivatives of tin, having the general formula $\text{SnR}_2(\text{OH})_2$, have not hitherto been obtained. Although the existence of such compounds might well be premised from the known relationship between tin and silicon, the only substances which have so far been produced by the hydrolysis of dihalogen derivatives of the type, SnR_2X_2 , are certain oxides of the composition SnR_2O . Further, the nature of these oxides is quite unknown.

Judging from the fact that all the silicon compounds of the composition $(\text{SiR}_2\text{O})_n$ which have been fully investigated (*loc. cit.*) have been shown to be fairly complex closed-chain compounds, it would seem highly probable that the corresponding tin derivatives have analogous structures. Since, moreover, even such moderately complex silicon compounds as trianhydrotris- and tetra-anhydrotetradiphenylsilicanediol are soluble in many of the ordinary organic solvents, whereas the tin compounds $(\text{SnR}_2\text{O})_n$ are insoluble, it might be inferred that the value of n in the latter case is greater than three or four.

The main objects of the work described in this paper were the preparation of some dihydroxystannic compounds of the composition $\text{SnR}_2(\text{OH})_2$, and the study of their relation to the corresponding oxides; it was believed that the results of such an investigation would throw some light, not only on the nature of these oxides, $(\text{SnR}_2\text{O})_n$, but also on the interesting problems presented by the stannic and metastannic acids.

The first point which we investigated was the possibility of preparing dihydroxydibenzylstannane, $\text{Sn}(\text{CH}_2\text{Ph})_2(\text{OH})_2$, by the hydrolysis of the corresponding dichloride (Smith and Kipping, T., 1912, 101, 2553). Although we failed to isolate the dihydroxy-derivative, we obtained some evidence of its existence, and in other respects the results were of considerable interest.

Dichlorodibenzylstannane is hydrolysed by a cold aqueous solution of potassium hydroxide, giving a soluble product, apparently a potassium derivative, $\text{Sn}(\text{CH}_2\text{Ph})_2(\text{OK})_2$ or



which is decomposed by carbonic or acetic acid, with separation of a colourless solid. This substance seems to be the dihydroxy-compound, $\text{Sn}(\text{CH}_2\text{Ph})_2(\text{OH})_2$, because, immediately after its pre-

cipitation, like dibenzylsilicanediol (Robison and Kipping, *loc. cit.*), it is rapidly and completely soluble in an aqueous solution of potassium hydroxide. The precipitate, however, very quickly changes; even by the time that it has been separated and washed, it has altered to such an extent that, when left in contact with a potassium hydroxide solution, about twenty-four hours elapse before it dissolves completely.

This behaviour of the supposed dihydroxystannic compound is analogous to that of diphenyl- and dibenzyl-silicanediols, both of which undergo condensation to some extent when they are precipitated from solutions of their potassium derivatives under conditions such as those just described; and although the change is much more pronounced in the case of the tin compound than in those of the silicon derivatives, it seems reasonable to infer that the three precipitated substances are all of the same type, and undergo fundamentally similar transformations. If so, it must be concluded that the freshly precipitated tin compound, which, from its method of formation and behaviour, is doubtless the dihydroxy-derivative, rapidly changes into some condensation product, analogous to one of the open- or closed-chain silicon compounds mentioned above.

On examination it was found at once that the precipitate differed fundamentally from all the known compounds of the composition SnR_2O , inasmuch as it was readily soluble in many organic solvents, such as benzene, ethyl acetate, chloroform, or carbon tetrachloride; from its solutions in all these and in several other organic liquids, it separated in well-defined, square tablets, which contained solvent, and which, when freed from the latter, melted at about $254\text{--}260^\circ$. The quantity of solvent in the crystals deposited from the four liquids just named could be expressed in certain molecular proportions (p. 2043).

Numerous analyses of the recrystallised, solvent-free substance gave results which showed clearly that the compound was not the dihydroxy-derivative $\text{Sn}(\text{CH}_2\text{Ph})_2(\text{OH})_2$, but which agreed with those required by a condensation product of the latter, having the formula:



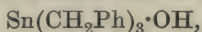
As, however, the compositions of successive condensation products differ but little from one another, and gradually approach very closely to that of the oxide, $\text{Sn}(\text{CH}_2\text{Ph})_2\text{O}$, the analytical results were not so conclusive as might have been desired.

Molecular-weight determinations by the cryoscopic method in benzene solution and also by the ebullioscopic method in chloroform solution, gave fairly concordant values of about 2700; these

agree with that required by a condensation product formed from 8 or 9 molecules of dihydroxydibenzylstannane, with elimination of 7 or 8 molecules of water respectively. The question arises, therefore, what weight is to be attached to these results?

Now in the case of the open-chain condensation products of diphenylsilicanediol, namely, anhydrobis- and dianhydrotris-diphenylsilicanediol, in both of which there is some independent evidence to confirm the result of the molecular-weight determinations (Kipping, T., 1912, 101, 2125), the average experimental value obtained in benzene solution was only about 30 per cent. higher than the calculated value; if, therefore, analogy is a safe guide in the present instance, it would seem that the results obtained in the case of the tin compound are also to be trusted.

This, however, is a new type of tin compound, and molecular-weight determinations with tin derivatives of even an approximately similar nature have not yet been published. We therefore examined dibenzylstannic acetate and tribenzylstannol,



in benzene solution, and found that whereas the experimental results agreed with the theoretical value in the case of the former, they were very much too high in that of the latter. The fact that this relatively simple monohydroxy-derivative is so largely associated in benzene solution renders it very probable that a dihydroxy-compound of the constitution:



would exhibit a similar behaviour; for this and other reasons the results of the analyses of the condensation product are clearly of much greater importance than those of the molecular-weight determinations.

It may therefore be concluded that the tin compound in question has the constitution just given, and is an analogue of dianhydrotris-diphenylsilicanediol; in accordance with this view it is named *dianhydrotris-dibenzylstannanediol*.

Although there may still be some doubt as to the constitution of the compound, we believe that there is conclusive evidence that it is an open-chain condensation product of dihydroxydibenzylstannane, and that the only point which is not quite decided is the number of molecules of the dihydroxy-compound which have condensed together.

This evidence is afforded by the behaviour of the compound when it is heated and when it is treated with a solution of potassium hydroxide. When heated alone at about 150–170°, or in boiling bromobenzene solution, it is converted with loss of the elements of water into an oxide, $[\text{Sn}(\text{CH}_2\text{Ph})_2\text{O}]_n$, which, like

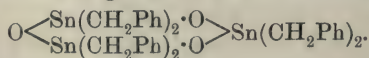
all the compounds of this type, is insoluble in all ordinary organic solvents, even in those of high boiling point.

Some attempts were made to determine the quantity of water formed during this transformation, but at the temperature required to bring about the conversion, dianhydrotris(dibenzylstannanediol) is readily oxidised, with the formation of benzaldehyde and dibenzyl, and even when it is heated in an atmosphere of carbon dioxide traces of these compounds are formed; apparently also a small proportion of the original substance is decomposed by the water which is formed during its conversion into the oxide, toluene being evolved. For these reasons the determinations were only approximately correct, and although the results agreed fairly well with those required for the conversion of a dianhydrobis(dibenzylstannanediol) into the corresponding oxide, they were not altogether satisfactory.

The insoluble oxide is also produced when the open-chain compound is left for some time in contact with a moderately concentrated solution of potassium hydroxide; further, it is deposited as a powder, together with dianhydrotris(dibenzylstannanediol), when a solution of the potassium derivative referred to above, in excess of potassium hydroxide solution, is kept for some days at the ordinary temperature in absence of air; also when dichlorodibenzylstannane is warmed with a concentrated solution of ammonium hydroxide.

All these methods of formation are analogous to those by which trianhydrotris- and tetra-anhydrotetraakis-diphenylsilicanediol are produced from the open-chain condensation products of diphenylsilicanediol (Kipping, T., 1912, 101, 2136, 2138).

The oxide, $[\text{Sn}(\text{CH}_2\text{Ph})_2\text{O}]_n$, melts and decomposes at 254—260°, that is to say, at the same temperature as the open-chain compound, which obviously is converted into the oxide below its melting point. The only evidence available on which to judge of the molecular formula of the oxide being its formation from the open-chain compound, it seems very probable that the oxide is a closed-chain condensation product of the following character:



At the same time it is not impossible that two (or more) molecules of the hydroxy-compound condense together to give a product containing a closed chain of six tin atoms and six oxygen atoms.

Attempts to find a solvent for the oxide led to the discovery that the compound is readily acted on by boiling quinoline, giving a brown solution; from this solution a very small proportion of

dianhydrotris(dibenzylstannanediol and a little tribenzylstannanol were isolated, but the main product was a resin, which yielded dichlorodibenzylstannane with acetone and hydrochloric acid.

A very small proportion of tribenzylstannanol is also formed when dianhydrotris(dibenzylstannanediol is heated alone at about 160° in an atmosphere of carbon dioxide, or with water at 180° . It is obvious from these and other instances that the hydrocarbon radicles attached to the tin atom are highly mobile; dichlorodiphenylstannane, for example, gives triphenylstannic chloride when it is merely treated with sodium amalgam or with a solution of ammonium hydroxide (Aronheim, *Annalen*, 1878, **194**, 145), and the compound $\text{CH}_2\cdot\text{SnO}_2\text{K}$ gives $[(\text{CH}_3)_2\text{SnO}]_n$ when it is warmed with alcoholic potash (Meyer, *Ber.*, 1883, **16**, 1442).

Experiments on the hydrolysis of dichlorodiphenylstannane and dichlorodi-*p*-tolylstannane failed to give a soluble compound analogous to dianhydrotris(dibenzylstannanediol; the only product in each case was a powder insoluble in all the neutral solvents which were tried, and having the composition of the oxide.

The results described in this paper point decidedly to the conclusion that dibenzylstannic oxide is a closed-chain compound of the molecular formula $[\text{Sn}(\text{CH}_2\text{Ph})_2\text{O}]_n$, where $n=3$ or some multiple of 3. From analogy it may be inferred that all the other dialkyl or diaryl stannic oxides have a similar constitution. Further, our results afford some experimental evidence in favour of the view that the acids supposed to have the composition H_2SnO_3 are highly complex condensation products of stannic hydroxide, $\text{Sn}(\text{OH})_4$, or are mixtures of such compounds, and that the relationship between the preparations usually known as the α - and the β -acids may be somewhat analogous to that between dianhydrotris(dibenzylstannanediol and dibenzylstannic oxide.

EXPERIMENTAL.

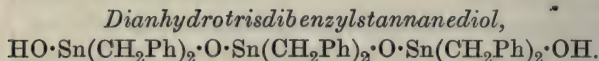
Hydrolysis of Dibenzylchlorostannane.

When finely-divided dibenzylchlorostannane (Smith and Kipping, T., 1912, **101**, 2553) is left in contact with a cold aqueous solution of potassium hydroxide, it gradually disappears, giving a soluble product, which is doubtless a potassium derivative, $\text{Sn}(\text{CH}_2\cdot\text{C}_6\text{H}_5)_2(\text{OK})_2$ or $\text{Sn}(\text{CH}_2\cdot\text{C}_6\text{H}_5)_2(\text{OK})(\text{OH})$. An approximately 7 per cent. solution of the alkali hydroxide seems to give the best results; when more concentrated solutions are used, the soluble potassium derivative which is first formed undergoes decomposition, an insoluble powder being deposited (see below).

From the clear alkaline solution, carbonic acid precipitates a colourless, somewhat flocculent solid, which, *immediately* after its

formation, is rapidly dissolved by a 7 per cent. solution of potassium hydroxide. This precipitate seems to undergo quickly some progressive change; thus, by the time it has been separated by filtration, and washed by the aid of the pump, it has altered to such an extent that it is only very slowly acted on by the alkali, and when it has been air-dried it is even more slowly attacked. Comparative experiments, under similar conditions, showed that freshly prepared, washed samples (about thirty minutes old), left in contact with a 5 per cent. potassium hydroxide solution, disappeared at the end of the second day, whilst the air-dried samples required about twenty-four hours longer.

A substance, apparently identical with that just described, is precipitated when the alkaline solution of the potassium derivative is cautiously treated with dilute acetic acid in quantity insufficient for neutralisation; also when finely-divided dibenzylstannane is triturated with a cold dilute aqueous solution of ammonium hydroxide, fresh quantities of the solution being added to the product until the latter is free from halogen.



The product, obtained by any of the three methods just described, washed with water, and roughly dried on porous earthenware, sinters at about 100° , and melts at about 250 — 260° , turning slightly brown; when washed with cold ether, which removes a small quantity of some resinous matter, the sample does not sinter at 100° , but melts at the same temperature as before; the sintering, therefore, is doubtless due to the presence of this resinous impurity, and not to the loss of the elements of water. The impurity in question is probably some product of atmospheric oxidation, as the originally colourless precipitate turns yellow superficially on exposure to the air. The air-dried precipitate, freed from the small proportion of resinous matter with the aid of ether or acetone, dissolves freely in cold benzene; when the solution is evaporated at the ordinary temperature, it deposits large, thick, square plates, which contain solvent, but which rapidly lose it on exposure to the air, giving a colourless powder; the latter melts at 254 — 260° , decomposing slightly, but, unlike the very finely-divided product obtained by precipitation, it does not seem to undergo atmospheric oxidation.

The following preparations of this compound were analysed, some having been obtained by methods described later:

I. and II. Different samples precipitated from alkaline solution

with carbonic acid, recrystallised from benzene, and kept in a vacuum until constant in weight.

III. A similar sample, which was washed with alcohol repeatedly after it had been crystallised from benzene.

IV. and V. Samples prepared by decomposing dichlorodibenzylstannanediol with ammonium hydroxide solution, crystallising from benzene, etc.

VI. Sample deposited from a solution in potassium hydroxide, crystallised from benzene, etc. (p. 2047).

I. 0.2520 gave 0.4753 CO_2 and 0.1008 H_2O . C=51.5; H=4.5.

II. 0.2013 „ 0.3818 CO_2 „ 0.0822 H_2O . C=51.8; H=4.5.

III. 0.1549 „ 0.2946 CO_2 „ 0.0635 H_2O . C=51.9; H=4.5.

IV. 0.2173 „ 0.4133 CO_2 „ 0.0871 H_2O . C=51.4; H=4.4.

V. 0.1602 „ 0.3029 CO_2 „ 0.0644 H_2O . C=51.7; H=4.5.

IV. 0.1851 „ 0.3506 CO_2 „ 0.0746 H_2O . C=51.6; H=4.5.

$\text{C}_{42}\text{H}_{44}\text{O}_4\text{Sn}_3$ requires C=51.9; H=4.6 per cent.

As the dihydroxy-derivative would contain 50.1 per cent. of carbon and 4.8 per cent. of hydrogen, whereas the oxide would contain 52.9 per cent. of carbon and 4.4 per cent. of hydrogen, it is obvious that the compound prepared by the above-described methods is neither of these substances. The average results agree best with those required by an open-chain condensation product formed from 3 molecules of dibenzylstannanediol with elimination of 2 molecules of water, but allowing for the usual experimental error, they would also agree passably with those required by the next higher condensation product of the same type.

The molecular weight of various preparations was determined in benzene solution by the cryoscopic method.

Substance. Grams.	Solvent. Grams.	$\Delta t.$	M.W.
0.511	14.8	0.062	2484
0.543	14.6	0.075	2482
0.563	14.8	0.077	2802
0.962	14.8	0.127	2562
0.975	14.6	0.130	2568
1.481	13.4	0.203	2666
1.635	14.8	0.185	2994

The compound is so sparingly soluble in cold phenol that this solvent could not be employed, but some determinations were made by the ebullioscopic method in chloroform solution.

Substance. Gram.	Solvent. c.c.	$\Delta t.$	M.W.
0.753	7.1	0.098	2811
0.753	7.9	0.088	2816
0.753	8.6	0.081	2806
0.753	9.1	0.073	2947

As the molecular weight of a dianhydrotris(dibenzylstannanediol

is only 969, experiments were made with dibenzylstannic acetate and also with tribenzylstannanol in benzene and in chloroform solutions in order to test the validity of the above results.

The acetate was examined by the cryoscopic method:

Substance. Gram.	Benzene. Grams.	$\Delta t.$	M. W.
0.225	12.4	0.203	427
0.488	12.4	0.405	487
0.684	12.4	0.545	505

The calculated molecular weight is 419.

The tribenzylstannanol was examined by the cryoscopic and by the ebullioscopic methods:

Substance. Gram.	Benzene. Grams.	$\Delta t.$	M. W.
0.257	17.7	0.110	660

Substance. Gram.	Chloroform. c.c.	$\Delta t.$	M. W.
0.314	6.4	0.162	786
0.314	7.3	0.144	784
0.314	8.6	0.125	759
0.314	9.5	0.102	841
0.992	9.7	0.367	727
0.992	10.4	0.32	775
0.992	10.7	0.297	813
0.992	11.3	0.280	821
0.992	11.7	0.269	813

The calculated value for the molecular weight is 409.

In view of the very high results obtained with the monohydroxy-derivative, it would seem that a dihydroxy-compound of the constitution of dianhydrotris(dibenzylstannanediol) might also give a very abnormal value; for this and other reasons it may be inferred that the condensation product described above has the constitution assigned to it, and that the molecular-weight determinations indicate association due to the presence of the two hydroxyl groups.

Dianhydrotris(dibenzylstannanediol) is very readily soluble in benzene, chloroform, or carbon tetrachloride, and dissolves freely in ethyl acetate, but is only sparingly soluble in cold ether or acetone, practically insoluble in alcohol or light petroleum, and insoluble in water. From the first four solvents just mentioned, and also from ethyl bromide or bromobenzene, the compound is deposited in crystals which contain solvent. All these crystals lose their solvent so rapidly on exposure to the air, even at the ordinary temperature, that the determination of their composition presents some difficulty, more especially when the crystals are small, as are those obtained from ethyl acetate and carbon tetrachloride solutions. In the case of these solvents, the freshly prepared crystals were rapidly pressed between layers of filter paper, placed in a weighing bottle, and weighed at intervals of about five minutes.

At first the loss in weight was very rapid, but as soon as the adherent solvent had evaporated, the rate of loss suddenly diminished, and the weight of the preparation at this break was taken to be that of the solvent-containing crystals. The samples were then kept under greatly diminished pressure; as the last traces of solvent were lost only very slowly, one or two days elapsed before a constant weight was reached.

Crystals from benzene: 0.684 lost 0.0833 or 12.2 per cent.

$3C_{42}H_{44}O_4Sn_3 \cdot 5C_6H_6$ requires 12.0 per cent.

Crystals from ethyl acetate: 1.207 lost 0.1162 or 9.98 per cent.

$3C_{42}H_{44}O_4Sn_3 \cdot 4CH_3 \cdot CO_2Et$ requires 10.7 per cent.

Crystals from chloroform: 0.852 lost 0.1536 or 17.9 per cent.

$3C_{42}H_{44}O_4Sn_3 \cdot 5CHCl_3$ requires 17.3 per cent.

Crystals from carbon tetrachloride: 0.920 lost 0.1567 or 17.0 per cent.

$3C_{42}H_{44}O_4Sn_3 \cdot 4CCl_4$ requires 16.9 per cent.

For the reason stated above, these results are not very trustworthy, and although the compositions of the various solvent-containing crystals are expressed by the above molecular proportions, others are not excluded.

Atmospheric Oxidation of Dianhydrotris(dibenzylstannanedio)l.

As some of the open-chain condensation products of diphenylsilicanediol and of dibenzylsilicanediol lose the elements of water and are converted into closed-chain condensation products when they are heated alone at a sufficiently high temperature, it seemed probable that dianhydrotris(dibenzylstannanedio)l would undergo a similar transformation; moreover, if the quantity of water formed in this process could be accurately determined, the results would afford evidence as to the constitution of the original substance.

Now when dianhydrotris(dibenzylstannanedio)l, crystallised from benzene and freed from solvent in a vacuum, is heated in the air at 100°, although it loses in weight, the loss is far greater than it would be if it were due to the elimination of water; thus at the end of two hours' heating, the loss amounted to 2.9 per cent.; at the end of a further six hours it was 6.4 per cent., and after six hours more 8.3 per cent. Even then there was no approach to a constant weight, and although the substance had turned brown and some of it had decomposed, it had not been converted into the closed-chain compound.

The loss in weight seems, in fact, to be entirely due to atmospheric oxidation, which results in the formation and subsequent volatilisation of benzaldehyde and dibenzyl; if the heating is carried out at about 115° in a glass tube, oily drops, smelling

strongly of benzaldehyde, are deposited on the colder portions of the glass.

When the freshly-crystallised compound is freed from solvent and heated at 100° in a stream of dried carbon dioxide, the loss in weight is practically negligible; if, however, the same sample is again heated (after it has been exposed to the air) a decrease of weight of something like 0.1 per cent. is observed, and losses of about the same amount continue to occur after each heating. As this loss is approximately the same each time, and does not vary appreciably and regularly with the period of heating, it is in all probability due to the effect of traces of oxygen, most of which are probably absorbed by the powder during its exposure to the air in the operation of weighing, etc.

Conversion of Dianhydrotris dibenzylstannanediol into the Oxide.

When a weighed quantity of pure dianhydrotris dibenzylstannanediol is heated at 100° in an atmosphere of dried carbon dioxide, a calcium chloride tube attached to the apparatus does not increase in weight appreciably, even after the substance has been heated during two hours. If then the temperature is raised to about 160° and kept between 160° and 170° for about an hour, water is evolved, and the increase in weight of the calcium chloride tube amounts to about 1.7 per cent. of the weight of the original substance; further, at this stage the soluble compound has been almost entirely transformed into a powder, which is insoluble in benzene. A further increase in weight of the calcium chloride tube (about 0.1 per cent. of the weight of the original substance) is observed if the temperature is then raised to and kept at 170 – 175° during about four hours, but this increase is probably not due to absorption of water.

It was thus proved that dianhydrotris dibenzylstannanediol undergoes a profound change at about 160° with liberation of water.

Unfortunately, the quantity of water evolved during this transformation could not be accurately determined, owing to the fact that towards the end of the operation, traces of oily products, as well as water, collect in the calcium chloride tube. So far as could be determined, the quantity was approximately 1.8 per cent. of the weight of the substance taken; at any rate, it did not exceed 2 per cent. As this loss corresponds approximately with the quantity, namely, 1.85 per cent., which would be formed in the conversion of a dianhydrotris dibenzylstannanediol into the corresponding oxide, the results of these experiments seem to confirm the analytical data, and to show that the substance has the constitution suggested.

Among the oily products collected in the calcium chloride tube, dibenzyl was identified, but doubtless the oil also contains benzaldehyde, and possibly toluene. These products seem to result from the action of traces of atmospheric oxygen, which it is practically impossible to exclude, and also from that of the water which is formed during the transformation of the soluble compound into the insoluble oxide; when it is borne in mind that 1 gram of oxygen might give rise to the formation of more than 11 grams of dibenzyl, and that the total gain in weight of the calcium chloride tube in the experiments just described is only about 0.03—0.04 gram, it is obvious that a minute quantity of oxygen might vitiate the results.

Action of Water on Dianhydrotris(dibenzylstannanedio)l.

In order to test the conclusion that the oily products obtained in the above-described experiments are formed, at any rate in part, by the action of the liberated water on dihydrotris(dibenzylstannanedio)l, some of this substance was heated with water and a little acetone at 180° during eight hours in a sealed tube. The substance had changed into a brown resin, and seemed to be completely decomposed. The contents of the tube were oily, and had a pronounced odour of toluene; from the brown resin, which was completely soluble in ether, and therefore free from stannic oxide, a small proportion of dibenzyl and a considerable proportion of tribenzylstannanol were isolated; the presence of dianhydrotris(dibenzylstannanedio)l in this product could not be established.

Dibenzylstannic Oxide, $[\text{Sn}(\text{CH}_2\text{Ph})_2\text{O}]_n$.

The compound obtained by heating dianhydrotris(dibenzylstannanedio)l alone, as described above, is not quite pure; it contains, at any rate in some instances, a relatively small proportion of tribenzylstannanol, which may be extracted with boiling benzene. The residue then consists of a practically colourless powder, which is insoluble in benzene and in all the common solvents. A sample was analysed with the following result:

0.1860 gave 0.3538 CO_2 and 0.0737 H_2O . $\text{C}=51.9$; $\text{H}=4.4$.

$\text{C}_{14}\text{H}_{14}\text{OSn}$ requires $\text{C}=53.0$; $\text{H}=4.45$ per cent.

This and other analyses show that the substance has the composition of a dibenzylstannic oxide; on treatment with a solution of hydrochloric acid in acetone, it is converted, apparently quantitatively, into dichlorodibenzylstannane.

From its method of formation, and for various other reasons, it would seem highly probable that this oxide is a closed-chain

compound, the molecule of which contains at least three atoms of tin.

The oxide turns yellow superficially on exposure to light and air, and when heated in the air at about 115° it undergoes oxidation, giving an oil, which smells strongly of benzaldehyde.

Conversion of Dianhydrotris-dibenzylstannanediol into the Oxide, $[\text{Sn}(\text{CH}_2\text{Ph})_2\text{O}]_n$, in Bromobenzene Solution.

As the soluble hydroxy-compound is converted into the insoluble oxide when it is heated alone at about 150 – 160° , it seemed probable that this change might also be brought about by heating a solution of the substance in some inert solvent; experiment showed that this inference was well founded.

Dianhydrotris-dibenzylstannanediol dissolves freely in cold bromobenzene, and when the solution is allowed to evaporate spontaneously it deposits colourless tablets, which contain solvent and effloresce on exposure to the air. When, however, the solution is heated at its boiling point on a reflux apparatus, it begins to deposit a colourless powder after a short time, and in the course of about half an hour practically nothing remains in solution.

This powder is insoluble in all the common solvents, and melts at 254 – 260° ; when treated with acetone and hydrochloric acid it gives dibenzylstannic chloride, apparently as the sole product. So far as could be ascertained, it was identical with the oxide prepared by heating dianhydrotris-dibenzylstannanediol alone, and an analysis of it gave the following result:

0.1815 gave 0.3494 CO_2 and 0.0721 H_2O . $\text{C}=52.43$; $\text{H}=4.41$.

$\text{C}_{14}\text{H}_{14}\text{OSn}$ requires $\text{C}=53.0$; $\text{H}=4.45$ per cent.

Action of Potassium Hydroxide Solution on Dianhydrotris-dibenzylstannanediol.

When dianhydrotris-dibenzylstannanediol is left in contact with a 15 per cent. solution of potassium hydroxide during some three days, a small proportion of it dissolves. The residue no longer consists entirely of the original substance; when washed, dried, and treated with benzene, a part of it dissolves, and the solution gives crystals of dianhydrotris-dibenzylstannanediol when it is allowed to evaporate. The insoluble portion melts at 254 – 260° , gives dichlorodibenzylstannane with acetone and hydrochloric acid, and is apparently identical with the insoluble oxide obtained by the other methods described above. A sample of the washed, insoluble product was analysed; the result was, however, not very satisfactory, possibly owing to the presence of occluded alkali:

0.1629 gave 0.3214 CO_2 and 0.0665 H_2O . $\text{C}=51.8$; $\text{H}=4.3$.

$\text{C}_{14}\text{H}_{14}\text{OSn}$ requires $\text{C}=53.0$; $\text{H}=4.45$ per cent.

The filtered potassium hydroxide solution slowly deposits a colourless powder when it is kept out of contact with the air, but even at the end of several days only a small proportion of the dissolved matter has been precipitated. The precipitate consists of a mixture of dianhydrotris dibenzylstannanediol and the insoluble oxide, which may be separated from one another in the usual manner.

The above-described alkaline solution, which doubtless contains the potassium derivative of dibenzylstannanediol, behaves in a manner analogous to that of an alkaline solution of diphenylsilicanediol; in both cases a mixture of condensation products of the diol is slowly deposited from the solution.

The insoluble oxide is also formed when dichlorodibenzylstannane is warmed with a concentrated aqueous solution of ammonium hydroxide; the colourless powder which is thus produced contains a small proportion of dianhydrotris dibenzylstannanediol, which is easily removed with the aid of benzene.

The insoluble oxide may be partly transformed into dianhydrotris dibenzylstannanediol with the aid of a 15 per cent. solution of potassium hydroxide; when left in contact with such a solution during some days, a small proportion dissolves, and from the filtered liquid dianhydrotris dibenzylstannanediol is precipitated on treatment with carbon dioxide.

Action of Boiling Quinoline on the Oxide.

When the insoluble oxide is boiled with quinoline, it disappears in the course of about ten minutes, giving a solution which is slightly coloured. If the quinoline is then separated by distillation in steam, there remains a solid residue, which is soluble in benzene. The benzene solution deposits crystals, melting at 124—125°, which were identified as those of tribenzylstannanol; on treatment with acetyl chloride they gave tribenzylstannic chloride. The benzene mother liquors, when diluted with light petroleum, gave a precipitate, from which a little dianhydrotris dibenzylstannanediol was isolated after prolonged fractional crystallisation, but the main product was a resin, which gave impure dichlorodibenzylstannane on treatment with acetone and hydrochloric acid.

Action of Boiling Benzyl Acetate on the Oxide.

Boiling benzyl acetate attacks the insoluble oxide, and after a very short time a colourless solution is obtained; if the solvent is then separated by distillation in steam, there remains a colourless solid, which dissolves freely in benzene. This solution deposits a finely crystalline powder, which melts at about 155—170°.

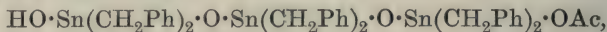
apparently without decomposing, and the melting point does not undergo any alteration, even after repeated crystallisation from benzene or from mixtures of acetone and benzene. On treatment with alcoholic hydrochloric acid, this substance gave dichlorodibenzylstannane:

0.2422 gave 0.4581 CO_2 and 0.1007 H_2O . $\text{C}=51.6$; $\text{H}=4.6$.

0.1813 „ 0.3426 CO_2 „ 0.0762 H_2O . $\text{C}=51.5$; $\text{H}=4.6$.

$\text{C}_{18}\text{H}_{20}\text{O}_4\text{Sn}$ requires $\text{C}=51.5$; $\text{H}=4.8$ per cent.

Although these percentages agree closely with those required by dibenzylstannic acetate, $\text{Sn}(\text{CH}_2\text{Ph})_2(\text{OAc})_2$, the last-named compound melts at $136\text{--}137^\circ$, and is different in other respects from the compound melting over the wide range given above. The results agree moderately well with those required by a hydroxyacetate derived from dianhydrotris(dibenzylstannanedio)l, and having the constitution:



as such a compound would contain 52.2 per cent. of carbon and 4.5 per cent. of hydrogen. As, however, the melting point was so very indefinite, the apparently homogeneous substance may have been a mixture; it was not further examined.

Diphenylstannic Oxide, $[\text{SnPh}_2\text{O}]_n$.

Diphenylstannic oxide has been prepared and examined by Aronheim (*Annalen*, 1878, **194**, 145), who obtained it by decomposing dichlorodiphenylstannane with alkalis; as it seemed possible that under suitable conditions the dichloride might give a condensation product analogous to dianhydrotris(dibenzylstannanedio)l, we made some experiments in this direction.

In the first place, tetraphenylstannane was prepared by the process employed by Pfeiffer and Schnurmann (*Ber.*, 1904, **37**, 321), and this compound was then converted into dibromodiphenylstannane by treatment with bromine according to a method described by Polis, which we carried out as follows: Tetraphenylstannane (1 mol.) is suspended in dry carbon tetrachloride, in which it is only sparingly soluble; the liquid is heated under a reflux apparatus, and bromine (2 mols.), mixed with carbon tetrachloride, is then slowly dropped down the condenser. At first the reaction takes place very rapidly, and the colour of the halogen disappears at once, but when nearly all the bromine has been added, the solution remains reddish-brown, even after it has been boiled for some time. When the reaction is at an end, the solution, which is quite free from suspended tetraphenylstannane, is submitted to distillation in steam in order to remove the carbon tetrachloride and bromobenzene. The tin compound which remains is treated with

a solution of sodium hydroxide, and the resulting oxide is separated by the aid of the pump, and washed with alcohol and ether. The product is then converted into dichlorodiphenylstannane by treatment with alcohol and hydrochloric acid.

The dichloride, purified by recrystallisation from alcohol, was cautiously hydrolysed with an ice-cold dilute solution of potassium hydroxide. It was thereby converted into a colourless powder, and the alkaline liquid, separated by filtration, gave no precipitate when treated with excess of carbon dioxide. In other experiments an alcoholic solution of the dichloride was slowly dropped into excess of an ice-cold, well-stirred, dilute aqueous solution of ammonium hydroxide; the product, so far as could be ascertained, was identical with that obtained by the first method, and it was insoluble in all the ordinary solvents.

This oxide, unlike the corresponding dibenzyl derivative, seems to be quite unchanged when it is left in contact with a 15 per cent. solution of potassium hydroxide, a fact which is the more noteworthy since phenyl derivatives are, as a rule, so much more strongly acidic than benzyl derivatives of similar constitution.

The diphenylstannic oxide was also unchanged when it was boiled with quinoline during some time.

Dichlorodi-p-tolylstannane, $\text{Sn}(\text{C}_6\text{H}_4\text{Me})_2\text{Cl}_2$.

This dichloride was prepared by methods analogous to those used in the case of the corresponding diphenyl derivative, starting with tetra-*p*-tolylstannane, which has been described by Pfeiffer (*Zeitsch. anorg. Chem.*, 1910, **68**, 102). The tetratolyl compound having been treated with bromine (2 mols.) in boiling carbon tetrachloride solution, the solvent and the bromotoluene were separated by distillation in steam, and the remaining tin compound was treated with excess of a solution of sodium hydroxide. The washed and dried oxide was first boiled with benzene in order to remove any unchanged tetratolylstannane, and then converted into the dichloride by treatment with alcohol and hydrochloric acid.

The alcohol was then evaporated, and the dichloride extracted with light petroleum; from this solution it was deposited in colourless plates, which were purified by recrystallisation from the same solvent:

0.4960 gave 0.3771 AgCl. $\text{Cl}=18.8$.

$\text{C}_{14}\text{H}_{14}\text{Cl}_2\text{Sn}$ requires $\text{Cl}=19.1$ per cent.

Dichlorodi-p-tolylstannane, like the corresponding diphenyl compound, is very readily soluble in all the ordinary organic solvents, but it crystallises well from light petroleum; it melts at $38-40^\circ$.

Di-p-tolylstannic Oxide, $[\text{Sn}(\text{C}_6\text{H}_4\text{Me})_2\text{O}]_n$.

The hydrolysis of the dichloride was carried out with a solution of potassium hydroxide and with ammonium hydroxide, exactly as described in the case of the diphenyl derivative; the only product which was thus obtained was a colourless solid, which did not melt at 300° , was insoluble in all the common solvents, and was reconverted into the dichloride on treatment with alcoholic hydrochloric acid:

0.1670 gave 0.3252 CO_2 and 0.0669 H_2O . $\text{C}=53.1$; $\text{H}=4.45$.

$\text{C}_{14}\text{H}_{14}\text{OSn}$ requires $\text{C}=52.9$; $\text{H}=4.4$ per cent.

These results seem to show that the dibenzyl compound which we have described as dianhydrotris(dibenzylstannanediol) has no analogue in the diphenyl and di-*p*-tolyl series; there is every reason to believe, however, that the diphenyl- and the di-*p*-tolyl-stannic oxides, like the corresponding dibenzyl compound, are closed-chain condensation products of the respective dihydroxy-compounds.

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CCXVII.—*Some Derivatives of Oleanol.*

By FRANK TUTIN and WILLIAM JOHNSON SMITH NAUNTON.

In a former communication (T., 1908, **93**, 896) Dr. Power and one of us described the isolation from olive leaves of a crystalline substance, which was designated oleanol. It was shown that oleanol possessed the formula $\text{C}_{31}\text{H}_{50}\text{O}_3$, and that it contained two hydroxyl groups, one of which had phenolic properties. Thus, on methylation with methyl iodide and sodium ethoxide, oleanol yielded a mono-methyl derivative, and the latter, on acetylation, gave a mono-acetyl compound. Oleanol itself was shown to afford a diacetyl derivative, which, on heating with dilute alcohol, lost one acetyl group, yielding monoacetyloleanol.

It was also shown (*loc. cit.*) that when diacetyloleanol (m. p. 208°) is heated above its melting point it underwent some change, gas being evolved, and a compound formed which did not melt at 310° . The analysis of the latter compound indicated it to possess the formula $\text{C}_{31}\text{H}_{48}\text{O}_3$, and, since it was not affected by alkalis, it

was concluded that it had been formed by the elimination of the two acetyl groups from diacetyloleanol.

More recently, Power and Moore (T., 1910, **97**, 1104) isolated from the leaves of *Prunus serotina* a substance isomeric with oleanol. This compound, which was strictly analogous to oleanol in its properties, was designated prunol. Diacetylprunol, on heating, underwent a change similar to that suffered by diacetyloleanol, but in this case it was conclusively shown that the reaction consisted in the elimination of one molecule of acetic anhydride from two molecules of the diacetyl compound. The product of high melting point (315°) has the composition $C_{66}H_{102}O_7$, but, since it is not affected by heating with alcoholic potassium hydroxide, it is probable that some change had occurred other than the condensation consequent upon the elimination of acetic anhydride.

A quantity of the alcoholic extract of olive leaves being available, it was considered of interest to pursue the investigation of oleanol with the hope of throwing some light on its constitution, and also to ascertain whether the behaviour of the diacetyl derivative on heating was analogous to that of diacetylprunol.

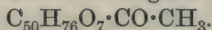
Although the amount of oleanol available did not permit of much information being gained regarding the constitution of a substance of so large a formula, a number of interesting derivatives have been prepared from it.

With regard to the change suffered by the diacetyl derivative on heating, it has now been ascertained that this reaction proceeds analogously to that undergone by diacetylprunol, and results in the formation of a substance possessing the formula $C_{66}H_{102}O_7$. The misleading analytical results previously obtained by Power and Tutin have been found to be due to the persistent retention of benzene, which was employed for the crystallisation of the compound in question.

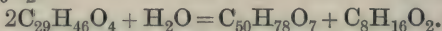
When oleanol, $C_{31}H_{50}O_3$, is oxidised with potassium permanganate in acetic acid solution it yields a dihydroxy-compound having the formula $C_{29}H_{46}O_4$. It would appear, therefore, that oleanol contains the group $CH_3 \cdot CH : C <$, and that this undergoes oxidation, yielding acetic acid and a ketone. Although no direct evidence of the ketonic character of the substance $C_{29}H_{46}O_4$ was obtained, it would appear certain that it contains a carbonyl group, and it is proposed to designate it *oleanone*. It yields *mono-* and *di-acetyl* derivatives.

The reactions which ensued on heating oleanone and diacetyloleanone with acetic acid containing water and hydrochloric acid respectively were of an unexpected nature, and serve to explain the considerable difficulty which was at first experienced in preparing any appreciable quantity of the first-mentioned compound.

Oleanone, when heated with glacial acetic acid, undergoes no change, but if the acid is slightly diluted with water a pink colour rapidly develops, which changes, first to green, and then to a dull violet colour, the latter gradually fading. On removal of the acetic acid a product is obtained which is uncrystallisable, but yields a crystalline *acetyl* derivative having the formula



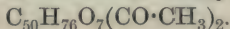
On hydrolysis, the latter yields the corresponding *alcohol*, $\text{C}_{50}\text{H}_{76}\text{O}_5(\text{OH})_2$. This change may be accounted for, empirically, by the condensation of 2 molecules of oleanone, accompanied by the addition of one molecule of water and the elimination of the elements $\text{C}_8\text{H}_{16}\text{O}_2$:



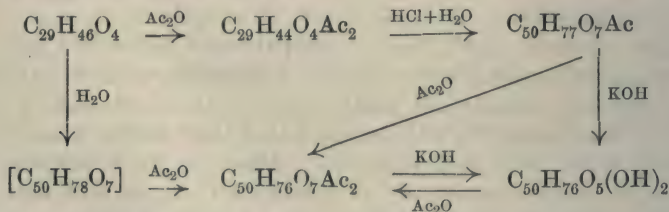
There are several ways possible in which such a change could occur, but the amount of material available was not sufficient to permit of the determination of the exact course of the reaction.

The above-described reaction is of interest inasmuch as the changes of colour closely resemble those produced by a phytosterol when treated with a drop of sulphuric acid in the presence of acetic anhydride. It is possible, therefore, that some similar condensation may take place in the case of the phytosterols.

When diacetyloleanone is heated with acetic acid containing aqueous hydrochloric acid, an analogous reaction occurs. The same change of colours takes place, and a *compound*, $\text{C}_{50}\text{H}_{77}\text{O}_7 \cdot \text{CO} \cdot \text{CH}_3$, results. The latter proved to be the monoacetyl compound corresponding with the above-mentioned diacetyl derivative,



On acetylation it yielded the latter, and on hydrolysis with alkali it gave the dihydroxy-compound, $\text{C}_{50}\text{H}_{76}\text{O}_5(\text{OH})_2$. These changes may be represented as follows:



The further oxidation of oleanone, $\text{C}_{29}\text{H}_{46}\text{O}_4$, could not be effected by means of potassium permanganate, and recourse was therefore had to the use of chromic acid. This resulted in the formation of a *substance*, $\text{C}_{29}\text{H}_{42}\text{O}_4$, and, since the latter yields only a *monoacetyl* derivative, it would appear that the alcoholic hydroxyl group originally present in oleanol had been oxidised to a keto-group. The other two atoms of hydrogen removed are possibly accounted

for by the oxidation of a reduced aromatic nucleus. When the substance, $C_{29}H_{42}O_4$, which melts at 275° , was submitted to the fairly prolonged action of alcoholic potassium hydroxide it was converted into an isomeride, melting at 315° . If, however, the action of the alkali was still more prolonged further, and more profound, changes occurred.

The direct oxidation of oleanol by means of a warm solution of chromic acid in acetic acid resulted in the formation of the above-mentioned compound, $C_{29}H_{42}O_4$, together with a mixture of carboxylic acids. It was ascertained that the latter contained at least three compounds, but no crystalline acid could be isolated from it.

EXPERIMENTAL.

The alcoholic extract of olive leaves from which the oleanol was obtained was the same as that employed for the investigation of the constituents of olive leaves (T., 1908, **93**, 891). It was mixed with water and distilled in a current of steam for the removal of the volatile constituents, after which the resin was separated from the aqueous liquid. The resin was then mixed with purified sawdust, and the thoroughly dried mixture extracted, first with petroleum (b. p. $35-50^\circ$), and then with ether. The ether extract consisted largely of crude oleanol, which separated as a green, sparingly soluble powder. The latter was collected, and crystallised from alcohol with the employment of animal charcoal, when pure oleanol was obtained in slender, colourless crystals, melting at 304° . The mother liquors from this substance gave further amounts of oleanol in an impure, amorphous condition, from which the pure compound was obtained by means of the acetyl derivative. The latter, on treatment with alcoholic potassium hydroxide, yielded pure oleanol.

Diacetyloleanol was first investigated with respect to its behaviour on heating. This derivative, after recrystallisation from acetic anhydride, melted at 208° . Determinations of its optical rotation and molecular weight gave the following results:

0.4636, made up to 20 c.c. with chloroform, gave $\alpha_D + 2^\circ 52'$ in a 2-dcm. tube, whence $[\alpha]_D + 61.9^\circ$.

0.5570, in 25.13 of benzene, gave $\Delta t - 0.26^\circ$. M.W. = 426.

$C_{35}H_{54}O_5$ requires M.W. = 554.

The somewhat low result of this molecular-weight determination may be accounted for by the great readiness with which diacetyloleanol undergoes partial hydrolysis.

A quantity (2 grams) of diacetyloleanol was heated in a distillation apparatus for some time at 240° , when a volatile substance was evolved, and collected in the receiver. This distillate was

identified by its general properties and boiling point as acetic anhydride. The solid residue in the distillation flask was dissolved in a small amount of hot petroleum (b. p. 90—120°), and boiling ethyl acetate added. A substance then separated in small, colourless, flattened prisms, which melted at 315—316°:

0.0995 * gave 0.2860 CO₂ and 0.0892 H₂O. C=78.4; H=10.0.

C₆₆H₁₀₂O₇ requires C=78.7; H=10.1 per cent.

It is thus evident that the change undergone by diacetyloleanol on heating is analogous to that suffered by diacetylprunol (Power and Moore, *loc. cit.*), and proceeds according to the following equation:



Oxidation of Oleanol with Potassium Permanganate.

Formation of Oleanone, C₂₉H₄₆O₄.

A quantity (10 grams) of oleanol was dissolved in glacial acetic acid, and a solution of 7 grams of potassium permanganate in a large volume of 95 per cent. acetic acid then gradually added. After keeping the mixture for an hour it was decolorised by means of sulphur dioxide, when, on pouring the solution into water, a quantity of solid was precipitated. The latter was isolated by means of ether, and the ethereal solution shaken with aqueous alkalis. This treatment, however, removed only acetic acid and relatively small amounts of amorphous products. The ethereal solution was then evaporated, and the residue crystallised from ethyl acetate. This was achieved only with considerable difficulty, owing to the great tendency of the product to separate in a colloidal condition. The material which had been once crystallised from ethyl acetate was then recrystallised several times from methyl alcohol, when it appeared to be dimorphous. It formed either glistening, colourless needles, or elongated, lustrous plates, both forms melting at 304°. The yield was about 40 per cent. of the weight of the oleanol employed:

0.1299 gave 0.3625 CO₂ and 0.1170 H₂O. C=76.1; H=10.0.

0.1331 „ 0.3712 CO₂ „ 0.1202 H₂O. C=76.0; H=10.0.

C₂₉H₄₆O₄ requires C=76.0; H=10.0 per cent.

It appears, therefore, that on oxidation oleanol suffers the loss of the elements C₂H₄ and the addition of one atom of oxygen. It is highly probable that the resulting product, C₂₉H₄₆O₄, is a ketone, although no oxime could be prepared from it, and it is proposed to designate it *oleanone*.

Oleanone is moderately soluble in most organic solvents, and a

* Dried at 130°.

determination of its optical rotatory power gave the following result:

0·3760, made up to 20 c.c. with chloroform, gave $\alpha_D + 1^\circ 31'$ in a 2-dcm. tube, whence $[\alpha]_D + 40\cdot4^\circ$.

Diacetyloleanone, $C_{29}H_{44}O_4(CO\cdot CH_3)_2$.—A quantity of oleanone was heated for some time with acetic anhydride, after which the mixture was poured into water, and the resulting solid collected. The latter was crystallised from a mixture of alcohol and ethyl acetate, when pure *diacetyloleanone* was obtained. This substance, like the corresponding dihydroxy-ketone, appears to be dimorphous. It forms either well-defined, colourless needles, or flat plates. Both forms melt sharply at 293° :

0·1371 gave 0·3682 CO_2 and 0·1173 H_2O . $C=73\cdot2$; $H=9\cdot5$.

$C_{33}H_{50}O_6$ requires $C=73\cdot1$; $H=9\cdot2$ per cent.

A determination of the specific rotatory power gave the following result:

0·3966, made up to 20 c.c. with chloroform, gave $\alpha_D + 2^\circ 27'$ in a 2-dcm. tube, whence $[\alpha]_D + 61\cdot8^\circ$.

Unlike diacetyloleanol, this diacetyl derivative does not undergo hydrolysis with the formation of a monoacetyl derivative when heated with 75 per cent. alcohol.

Monoacetyloleanone, $C_{29}H_{45}O_4\cdot CO\cdot CH_3$.—A considerable quantity of impure material contained in the mother liquors from the crystallisation of crude diacetyloleanone was fractionally crystallised, when, in addition to the last-mentioned compound, a small amount of another substance was obtained. The latter formed well-defined, colourless needles, melting at 260° :

0·1038 gave 0·2831 CO_2 and 0·0878 H_2O . $C=74\cdot4$; $H=9\cdot4$.

$C_{31}H_{48}O_5$ requires $C=74\cdot4$; $H=9\cdot6$ per cent.

This substance thus appeared to be *monoacetyloleanone*, and, when hydrolysed with alcoholic potassium hydroxide, oleanone was regenerated from it. It is more soluble in alcohol and less so in ethyl acetate than the corresponding diacetyl derivative, but is freely soluble in chloroform. Its optical rotatory power was determined with the following result:

0·4147, made up to 20 c.c. with chloroform, gave $\alpha_D + 3^\circ 3'$ in a 2-dcm. tube, whence $[\alpha]_D + 73\cdot5^\circ$.

When the ketone was regenerated from either of its acetyl derivatives the product obtained usually consisted of a mixture of the above-mentioned dimorphous forms.

Action of Dilute Acetic Acid on Oleanone.

The oxidation of oleanol necessitated the use of a large volume of acetic acid (3 litres for 10 grams of the alcohol), and this was

also inconvenient for the isolation of the oxidation product. In a number of experiments, therefore, it was sought to recover the greater part of the acetic acid by distillation in a vacuum before the reaction mixture containing the oxidation product had been poured into water. When this was done, however, it was found very difficult, or impossible, to isolate any pure oleanone from the oxidation product, the latter being, for the most part, uncrystallisable. It was thus evident that the evaporation of the acetic acid with the aid of heat had caused some change to take place, and it was at first thought that this might be due to the partial acetylation of the oxidation product by the acetic acid in the presence of the manganous sulphate which had been formed during the treatment of the oxidation mixture with sulphur dioxide. A quantity (1 gram) of pure oleanone was therefore dissolved in acetic acid, and such an amount of manganous sulphate added, dissolved in a little water, as would have been formed during the preparation of one gram of oleanone. The mixture was boiled for three hours, after which it was concentrated in a vacuum and poured into water. The product was then extracted with ether, when some yellow, uncrystallisable material was obtained. The latter was heated for some time with acetic anhydride, after which the mixture was poured into water, and the resulting solid collected. The latter was crystallised several times from dilute alcohol, when small, colourless plates were obtained, which, on heating, first softened, and then melted at 324° . This substance was evidently a new compound, being quite distinct from diacetyloleanone, and it was thus evident that heating with acetic acid and manganous sulphate did not cause simply partial acetylation, as had been thought, but that some more profound change had occurred.

The action of anhydrous acetic acid alone on oleanone was therefore investigated, but, after boiling for several hours, the original ketone could be recovered unchanged. When, however, a small amount of water was added to a solution of oleanone in boiling glacial acetic acid, a pink colour rapidly developed, which gradually changed to green, and finally to a faint violet tint. On isolating the resulting product, only uncrystallisable material was obtained, but, on acetylation, the latter yielded the above-described acetyl derivative, melting at 324° . It is evident, therefore, that oleanone is radically changed by the action of hot dilute acetic acid.

The *diacetyl* derivative, $C_{50}H_{76}O_7(CO \cdot CH_3)_2$ (m. p. 324°), was moderately soluble in alcohol and ethyl acetate, but more readily so in chloroform or benzene. After drying at 125° , it yielded the following results:

0.1537 gave 0.4164 CO_2 and 0.1308 H_2O . $\text{C}=73.9$; $\text{H}=9.4$.

0.1067 „ 0.2896 CO_2 „ 0.0922 H_2O . $\text{C}=74.0$; $\text{H}=9.6$.

0.5208, in 24.0 of benzene, gave $\Delta t -0.13^\circ$. $\text{M.W.}=853$.

$\text{C}_{54}\text{H}_{82}\text{O}_9$ requires $\text{C}=74.1$; $\text{H}=9.4$ per cent. $\text{M.W.}=874$.

A quantity of the acetyl derivative was hydrolysed by means of alcoholic potassium hydroxide, and the resulting substance isolated. The latter was crystallised from ethyl acetate containing a small amount of alcohol, when it separated in very thin, colourless plates, which melted at 312° :

0.1028 gave 0.2814 CO_2 and 0.0926 H_2O . $\text{C}=74.7$; $\text{H}=10.0$.

$\text{C}_{50}\text{H}_{78}\text{O}_7$ requires $\text{C}=74.7$; $\text{H}=9.9$ per cent.

Action of Acetic and Hydrochloric Acids on Diacetyloleanone.

A quantity (4 grams) of diacetyloleanone was dissolved in glacial acetic acid, and 15 per cent. hydrochloric acid added to the hot liquid until a faint cloudiness was produced. The mixture was then boiled for some time, when the previously-described cycle of colour changes occurred, at the completion of which a substance separated from the boiling liquid in colourless, glassy plates. After recrystallisation from methyl alcohol, this substance melted at 332° :

0.1417 gave 0.3904 CO_2 and 0.1226 H_2O . $\text{C}=75.2$; $\text{H}=9.6$.

0.1316 „ 0.3626 CO_2 „ 0.1154 H_2O . $\text{C}=75.2$; $\text{H}=9.7$.

$\text{C}_{52}\text{H}_{80}\text{O}_8$ requires $\text{C}=75.0$; $\text{H}=9.7$ per cent.

This compound proved to be the *monoacetyl* derivative of the previously-described dihydroxy-compound, melting at 312° . On hydrolysis with alcoholic potassium hydroxide it yielded the latter, and on acetylation it gave the diacetyl derivative. (Found, $\text{C}=74.1$; $\text{H}=9.6$. Calc., $\text{C}=74.1$; $\text{H}=9.4$ per cent.) The melting point of the diacetyl derivative when prepared in this manner, however, could not be raised above 292° , but this was doubtless due to the persistent retention of a very small amount of impurity. In all other respects the two preparations were identical, and no lowering of the melting point occurred on mixing them.

Oxidation of Oleanone with Chromic Acid.

As oleanone could not be further oxidised by means of potassium permanganate, recourse was had to the use of chromic acid.

A quantity (10 grams) of oleanone was dissolved in 1 litre of glacial acetic acid, and a solution of 13 grams of chromic acid in 150 c.c. of 75 per cent. acetic acid gradually introduced, the mixture being stirred, and maintained at $55-60^\circ$. Sulphur dioxide was

then passed into the mixture to remove any excess of chromic acid, and the solution poured into water. The mixture was subsequently extracted with ether, and the ethereal solution deprived of acetic acid by means of aqueous potassium hydroxide, washed, dried, and concentrated. A sparingly soluble, crystalline substance then separated from the solution. This was most conveniently recrystallised by extraction with ether in a Soxhlet apparatus, when it formed thin, lustrous, colourless plates, melting at 275° . The yield of pure material was 4.5 grams from 10 grams of oleanone:

0.1272 gave 0.3586 CO_2 and 0.1062 H_2O . $\text{C}=76.9$; $\text{H}=9.3$.

0.1357 „ 0.3811 CO_2 „ 0.1151 H_2O . $\text{C}=76.6$; $\text{H}=9.4$.

$\text{C}_{29}\text{H}_{42}\text{O}_4$ requires $\text{C}=76.7$; $\text{H}=9.3$ per cent.

This *compound* is thus seen to be formed from oleanone by the loss of 4 atoms of hydrogen. It was found to contain only one hydroxyl group, and is probably a diketone.

A small quantity of the substance $\text{C}_{29}\text{H}_{42}\text{O}_4$ was acetylated by means of acetic anhydride, and the product crystallised from absolute alcohol. Long, colourless, hair-like needles were then obtained, which melted at 268° :

0.1027 gave 0.2815 CO_2 and 0.0842 H_2O . $\text{C}=74.8$; $\text{H}=9.1$.

0.3404, in 23.56 of benzene, gave $\Delta t -0.147^{\circ}$. M.W.=492.

$\text{C}_{31}\text{H}_{44}\text{O}_5$ requires $\text{C}=75.0$; $\text{H}=8.9$ per cent. M.W.=496.

This *monoacetyl* derivative is moderately soluble in alcohol, somewhat more so in ethyl acetate, and readily so in chloroform or benzene.

Action of Potassium Hydroxide on the Compound $\text{C}_{29}\text{H}_{42}\text{O}_4$.

The substance $\text{C}_{29}\text{H}_{42}\text{O}_4$ could be recovered unchanged after being heated for a short time with fairly dilute alcoholic potassium hydroxide, and it could therefore be regenerated from its acetyl derivative. When, however, stronger alkali was employed, and the heating was more prolonged, further changes took place.

A quantity of the substance $\text{C}_{29}\text{H}_{42}\text{O}_4$ (m. p. 275°) was dissolved in fairly concentrated alcoholic potassium hydroxide, and the mixture heated for two hours. The liquid was then poured into water, acidified, and extracted with ether. On evaporation of the ether a product was obtained, which, when crystallised from a mixture of ethyl acetate and alcohol, separated in small, thin prisms, melting at 315° . The yield of the latter was by no means quantitative, and the mother liquors contained uncrystallisable material:

0.1017 gave 0.2867 CO_2 and 0.0849 H_2O . $\text{C}=76.9$; $\text{H}=9.3$.

0.1406 „ 0.3970 CO_2 „ 0.1182 H_2O . $\text{C}=77.0$; $\text{H}=9.3$.

$\text{C}_{29}\text{H}_{42}\text{O}_4$ requires $\text{C}=76.7$; $\text{H}=9.3$ per cent.

This substance therefore appears to be isomeric with the compound $C_{29}H_{42}O_4$ (m. p. 275°), from which it was obtained. A mixture of the two isomerides melted at $250\text{--}256^\circ$.

The new isomeride, melting at 315° , yielded a *monoacetyl* derivative on treatment with acetic anhydride. This derivative crystallised from ethyl acetate in colourless needles, melting at 308° :

0.1106 gave 0.3046 CO_2 and 0.0920 H_2O . $C=75.1$; $H=9.2$.

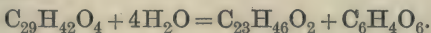
$C_{31}H_{44}O_5$ requires $C=75.0$; $H=8.9$ per cent.

Another portion of the original compound, $C_{29}H_{42}O_4$ (m. p. 275°), was dissolved in concentrated alcoholic potassium hydroxide, and the mixture boiled for three days, after which it was evaporated almost to dryness. The residue was then poured into water, acidified, and extracted with ether. On evaporating the ether a product was obtained, from which neither of the isomeric substances, $C_{29}H_{42}O_4$, could be obtained, and which was, for the most part, uncrystallisable. It yielded, however, a small amount of a substance, which crystallised in small leaflets, melting at $87\text{--}88^\circ$, and had the characters of a higher fatty acid:

0.0578 gave 0.1652 CO_2 and 0.0682 H_2O . $C=78.0$; $H=13.1$.

$C_{23}H_{46}O_2$ requires $C=78.0$; $H=13.0$ per cent.

The formation of a fatty acid, $C_{23}H_{46}O_2$, from the substance $C_{29}H_{42}O_4$ would account for the major portion of the molecule of oleanol, and would greatly facilitate the elucidation of the constitution of the latter. The change might take place according to the following equation:



Unfortunately, however, this point cannot be considered as definitely established, since the amount of material available only permitted of one further small experiment being conducted, and the latter did not result in the isolation of any more of the fatty acid in question. It is difficult to see, however, how the acid $C_{23}H_{46}O_2$ (m. p. $87\text{--}88^\circ$) could have been introduced from an extraneous source, particularly as no compound possessing this composition and melting point has hitherto been known. An acid possessing the same formula, but melting at 68° , has been shown to occur in olive leaves (Power and Tutin, *loc. cit.*), but it is impossible for any of this to have been occluded in the compound $C_{29}H_{42}O_4$ (m. p. 275°), which was hydrolysed, since the latter was prepared from pure oleanol, melting at 304° .

The action of concentrated alcoholic potassium hydroxide on oleanol itself was investigated, but was found to bring about no change.

Oxidation of Oleanol with Chromic Acid.

Oleanol was oxidised with chromic acid under the same conditions as those described in connexion with the oxidation of oleanone. At the completion of the oxidation the acetic acid solution was poured into water and extracted repeatedly with ether. The ethereal solution was then shaken with aqueous alkali, which removed acetic acid and a considerable amount of a mixture of solid carboxylic acids. The ethereal liquid then contained the above-described substance, $C_{29}H_{42}O_4$ (m. p. 275°), the yield of which was about 10 per cent. of the weight of the oleanol employed.

The above-mentioned mixture of carboxylic acids could not be crystallised, nor could any crystalline ester or salt be obtained from it. It was therefore converted into the barium salt, and the latter precipitated in seven fractions by concentrating its aqueous solution. The acid was then recovered from each of the fractions of barium salt, and the resulting products, all of which were amorphous, dried at 125° . Their analysis and the determination of their neutralisation values gave the following results:

Fraction.	Percentage of carbon.	Percentage of hydrogen.	Neutralisation value.
1	69.0	8.4	236
2	68.6	8.3	237
3	71.7	8.6	268
4	70.7	8.6	268
5	69.4	8.5	243
6	69.7	8.4	230
7	68.3	8.0	221

It is thus evident that the direct oxidation of oleanol by means of chromic acid results in the formation of at least three carboxylic acids, in addition to the above-described substance, $C_{29}H_{42}O_4$.

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CCXVIII.—*The Interaction of Sodium Amalgam and Water.*

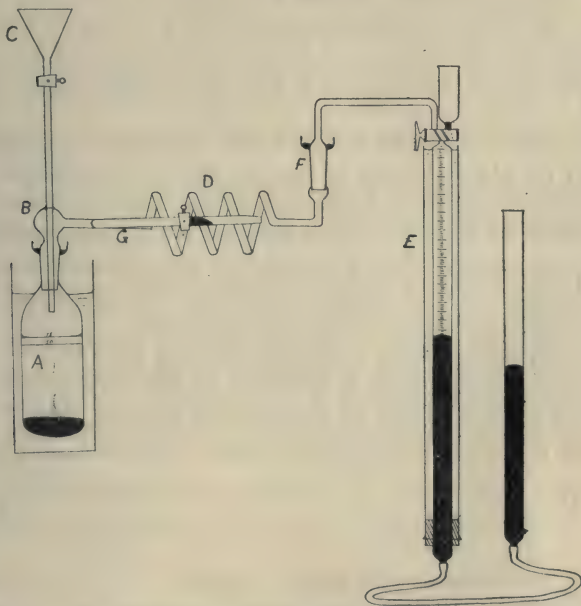
By HERBERT BRERETON BAKER and LESLIE HENRY PARKER.

THE fact that water prepared under special conditions acted with a strikingly slower velocity on sodium amalgam than did ordinary distilled water was observed by one of us two years ago (Baker, *Trans. Faraday Soc.*, 1910–11, **6**, 119). The original qualitative experiment was performed in the following manner.

Water was distilled from a copper or Jena-glass boiler, and the

steam passed through a carefully cleaned copper tube, made without brazing, which acted as a condenser. Two or three inches of the copper tube were heated to redness by a Bunsen burner before the steam was condensed. The tube was suitably bent to prevent any spray from the boiler being collected in the receiver. For the purpose of the experiments, after about one-sixth of the quantity of water taken had been distilled over, the distillate was collected, the distillation being stopped when a similar quantity was left in the boiler. Two Jena-glass test-tubes were then cleaned with a mixture of nitric and chromic acids, rinsed, and steamed for half-

FIG. 1.



an-hour. One was half-filled with this special water, and the other with ordinary distilled water. Into each a few c.c. of sodium amalgam were filtered through a dried filter paper, pierced with small holes.

Whilst the action in the tube containing ordinary distilled water spread very quickly over the surface of the amalgam, and hydrogen was evolved at a rapid rate, in the case of the specially distilled water the action was confined practically to one small point on the surface of the amalgam, and the hydrogen was evolved as a fine stream, at an obviously slower rate than in the case of the ordinary distilled water. An apparatus (Fig. 1) was then constructed to measure accurately the volume of gas evolved.

A is the reaction-vessel, which consisted of a large, thick Jena-glass test-tube, with its neck drawn out, into which was ground the open stopper *B*, of soft glass.

Through *B* was sealed the tap-funnel *C*, the upper portion of which was made conical to accommodate a filter paper. Into *B* was also sealed the worm *D*, to give flexibility to the apparatus. Between *B* and *D* a side-tap *G* was inserted, to allow an independent opening to the atmosphere when necessary. The whole was then put in connexion with the nitrometer *E*, by means of the ground joint *F*. The two ground joints and the tap *G* were protected by mercury seals. The mode of carrying out the experiment was to put a quantity of the water into *A*, fit the apparatus together, and filter in the amalgam through *C*. The reaction-vessel was graduated for 50 c.c. and 55 c.c., and except where otherwise stated, 50 c.c. of water and 5 c.c. of amalgam were taken for the test.

Before each experiment, the whole apparatus was cleaned as described for the test-tubes in the qualitative experiment.

The reaction-vessel and the nitrometer were surrounded with water jackets to keep them at as constant a temperature as possible. All the experiments were conducted at the ordinary temperature, and leaks were proved absent by leaving the apparatus together, empty, overnight, under diminished pressure.

As a comparison, below is a table showing the rates of evolution of hydrogen, firstly, from a specimen of ordinary distilled water, secondly from a specimen of the specially distilled water.

Time in hours.	Ordinary distilled water.	Specially distilled water.
1	23.7 c.c. H ₂	1.4 c.c. H ₂
2	—	2.6
3	54.0	—
4	—	—
5	—	4.0
6	77.0	—
7	—	4.6

The temperature of reaction in each case was 10°.

Between the times at which the readings were taken, the pressure in the apparatus was kept at about 20 mm. under atmospheric pressure. The results obtained seemed of sufficient interest to justify more detailed investigation.

The special water was prepared in quantity by distillation from a copper boiler made without brazing, with a copper condenser screwed into the top. The water was stored in a Jena-glass bottle fitted with a siphon tap, and protected by a soda-lime tube. The water could be stored in this way for a week or more without much alteration of its activity.

The sodium amalgam for use in these experiments was prepared

with redistilled mercury, and it contained rather less than 1 per cent. of sodium.

As a check on the reaction, after the reaction had been going on for some time, the apparatus was quickly disconnected, and 25 c.c. of the solution drawn out at once, and titrated with standard hydrochloric acid solution.

It was noted at first that the alkalinity of the solution always corresponded with a volume of hydrogen in excess of that actually measured.

Experiment.	Time in hours.	c.c. H ₂ observed.	c.c. H ₂ calculated from titration.
<i>A</i>	19	52.5	70.2
<i>B</i>	20½	21.8	25.8
<i>C</i>	6	3.1	33.9

No leak could be detected in the apparatus by further testing, and also during the course of the reaction the pressure was kept below that of the atmosphere, so that any leak would have been a leak *inwards*.

It was then thought that the excess volume of gas indicated by the titration might be due to the original alkalinity of the amalgam itself.

To test this, a few c.c. of the amalgam were shaken for a few seconds with about 10 c.c. of the special water in a tap-funnel. No visible action took place in this short time, so that the water gained no alkalinity from direct action on the amalgam. The water was separated off and titrated, and in spite of the small quantity of amalgam taken, showed an alkalinity corresponding with 0.6 c.c. of hydrogen.

It was then thought advisable to filter the amalgam as efficiently as possible, and specially cleaned asbestos was chosen as the filtering agent.

Asbestos wool was allowed to soak for twenty-four hours in a mixture of concentrated hydrochloric and nitric acids. It was then thoroughly washed with distilled water until the latter showed no acid reaction, and then heated in a muffle furnace for several hours.

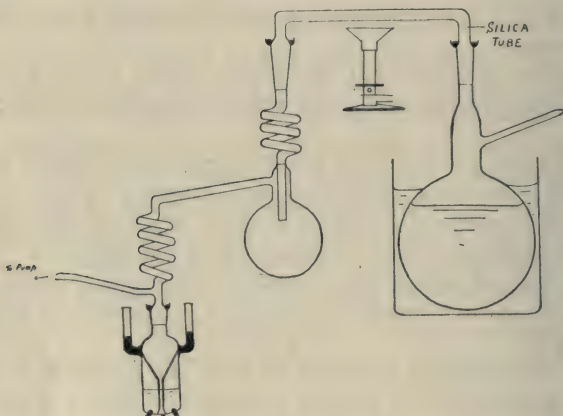
The tap-funnel *C* in the apparatus described above was then replaced by a glass tube of about 8 mm. diameter, lightly packed with the asbestos, the latter held in place at a constriction at the lower end by a roll of filter paper. To the upper end of this filtering column was sealed a wider portion, fitted with a ground stopper. The amalgam was filtered in through a punctured filter paper, and the stopper quickly inserted. This form of the apparatus also had the advantage of abolishing the unprotected tap in the tap-funnel.

The effect of this was to diminish the discrepancy between the observed volume of gas and that calculated from the titration, although not to eliminate it entirely.

Experiment.	Time in hours.	c.c. H ₂ observed.	c.c. H ₂ calculated from titration.
<i>A</i>	4	2.9	4.5
<i>B</i>	6	27.6	34.7
<i>C</i>	6	4.0	4.7
<i>D</i>	4	10.8	11.8
<i>E</i>	2	5.3	5.3
<i>F</i>	6	6.0	6.0

The next point thought to be of importance to the investigation was to determine whether the rate of action of the water on the amalgam was any sort of function of the conductivity.

FIG. 2.



For this purpose different specimens of water were obtained from various sources.

The conductivities were measured in a specially made cell of Jena-glass having a capacity of about 75 c.c., containing platinum plates about 1 cm. \times 2 cm. and 1 mm. apart.

The cell was supplied with a tube ground into the neck, so that it could be sealed off if necessary when distilling in a vacuum. It was not found possible to obtain water of much less than 1 gemmho conductivity, as a general rule; this was possibly due to the London atmosphere. Even by distilling in a vacuum, water of much less conductivity than this was not obtained. It was thought that light might be thrown on the cause of the inactivity of the water by testing water which had been subjected to different methods of treatment.

Except where otherwise stated, ordinary distilled water was placed in the boiler.

Specimens of water were obtained as follows:

(1) From the copper boiler and condenser as described above. This gave water varying in conductivity from 0.7 gemmho to 2.5 gemmhos.

(2) Water kindly supplied by Mr. Bousfield from his special still. This on reaching us had a conductivity of about 1.8 gemmho.

(3) From a specially modified Bousfield still (Fig. 2), made throughout of Jena-glass, except that a silica tube was fitted into the apparatus by mercury-protected ground joints, in passing through which the steam was heated to redness.

In collecting the water for conductivity determinations, the cell was surrounded by ice, and the distillation carried out in a vacuum just above the ordinary temperature. A little potassium hydrogen sulphate was placed in the boiler. This gave water of about 1.7 to 1.9 gemmhos conductivity.

(4) A large platinum still was used of a capacity of about 1 litre, and the various parts could be screwed together without the use of any extraneous material.

A current of air freed from carbon dioxide was passed in through the still-head. The condensed steam was received either in a platinum bottle or in the reaction vessel itself, which was protected by a soda-lime tube, so that the water was distilled and collected in an atmosphere free from carbon dioxide. This gave water varying in conductivity from 1 to 2 gemmhos. Superheating the steam at the still-head, either by a Bunsen burner or by means of an electric furnace surrounding it, did not alter the conductivity to any appreciable extent.

The following table, arranged in order of increasing conductivity, shows that there is no regular relation between the activity of a

Source of water.	Conductivity $\times 10^{-6}$.	Activity in c.c. H_2 per hour.
Platinum still	1.08	2.9
Modified Bousfield still	1.3	1.7
Copper still	1.38	10.8
Copper still	1.38	1.4
Platinum still	1.48	1.9
Modified Bousfield still	1.76	1.5
Mr. Bousfield	1.86	3.2
Platinum still	1.86	0.63
Modified Bousfield still	1.9	1.3
Platinum still	2.08	1.0
Platinum still	2.17	2.4
Copper still	2.31	1.4
Platinum still	3.6	5.1
Copper still	3.8	1.0
—	4.4	2.8
Copper still	12.9	1.2

specimen of water on the amalgam and its conductivity, although, as a general rule, the purer waters were less active.

Some of the specimens of water had been submitted to special treatment, such as exposure to metals, radium bromide, etc., the individual effects of which it is hoped to describe in a further communication.

That one of the main factors in the decrease of activity was the superheating of the steam is shown by the following tables:

Time in hours.	1.	2.	3.	4.	5.	6.
c.c. H_2 from dis-	1.2	3.3	5.2	7.0	9.3	—
tilled water re-	0.46	2.2	4.0	5.5	7.9	—
distilled, steam	3.24	7.7	9.9	12.5	14.3	17.6
not superheated.	2.3	5.1	8.7	11.0	12.0	—
c.c. H_2 from dis-	0.5	1.3	1.8	2.9	—	—
tilled water re-	1.0	1.7	2.5	3.0	3.9	4.0
distilled, steam	0.46	1.3	2.6	3.0	4.3	5.8
superheated.	0.28	1.1	2.03	2.9	3.3	—
	unmeasurable	0.6	1.3	—	2.1	3.0

The reason for this decrease in activity was still obscure. The supposition that the inactive water might be (H_2O) molecules associated to a greater extent than in the case of ordinary active water, was rather discounted by the fact that the boiling and freezing points of this water were not sensibly different from those of ordinary distilled water.

The effect of the reduction of pressure on the reaction was then tried, the reaction-apparatus being exhausted through the tap *G*, and the readings taken at constant volume at a fixed point on the nitrometer. Knowing the internal volume of the apparatus to this point, and measuring the difference in level of the mercury in both limbs of the nitrometer, the volume of gas given off over a definite period could be calculated.

Experiments under diminished pressure.					Comparative experiments, ordinary pressure throughout.	
Experi- ment.	Time in hours.	Average pressure. mm.	c.c. H_2 .	Difference per hour in c.c. H_2 .	c.c. H_2 .	Difference per hour in c.c. H_2 .
A.	1	132	7.3	7.3	2.2	2.2
	2	260	13.5	6.2	9.4	7.2
	3	348	16.6	3.1	14.6	5.2
	4	397	18.7	2.1	17.8	3.2
	5	430	20.1	1.4	19.7	1.9
	6	454	21.3	1.2	21.2	1.5
B.	1	138	8.1	8.1	unmeasurable	unmeasurable
	1½	259	13.1	5.0	0.9	0.9
	3	384	21.4	8.3	2.6	1.7
	4	510	26.7	5.3	3.4	0.8
	5	587	29.8	3.1	4.2	0.8
	6	630	31.9	2.1	4.9	0.7

Experiments under diminished pressure.					Comparative experiments, ordinary pressure throughout.	
Experi- ment.	Time in hours.	Average pressure. mm.	Difference per hour in c.c. H ₂ .			Difference per hour in c.c. H ₂ .
	1	121	7.6	7.6	0.3	0.3
	2	258	14.7	7.1	1.8	1.5
	3	386	21.4	6.7	2.8	1.0
	4	488	25.8	4.4	3.2	0.4
	5	570	29.0	3.2	3.7	0.5
	6	612	31.5	2.5	4.1	0.4
D.	1	242	20.1	20.1	0.8	0.8
	2	445	21.9	1.8	2.3	1.5
	3½	471	22.8	0.9	3.1	0.8
	4½	484	23.2	0.4	3.8	0.7
	5½	491	23.6	0.4	4.1	0.3
	6½	498	23.9	0.3	4.6	0.5

It will be seen from this table that whilst the action proceeded with moderate regularity while under constant pressure, in the case of the experiments under diminished pressure the rate decreased as the pressure in the apparatus increased, until as the pressure more nearly approached that of the atmosphere, so the rate of action became more and more comparable with that of the comparative experiment carried out under the ordinary pressure.

In this connexion, another important point that was noticed was the fact that whenever the reaction was progressing quickly, for instance, under low pressure, the action was taking place all over the surface of the amalgam; but the slower the rate, the more limited became the area of activity, until with the least active specimens of water, under the best conditions, the action was confined to a small point about the centre of the surface of the amalgam.

A possible explanation of these facts was the supposition that a film of hydrogen was formed over the surface of the amalgam, which protected it more or less from the action of the water; and that, in the case of the less pure waters, by some means or other this film was removed or ruptured. Also the explanation of the localised action might be found in assuming some small impurity in the amalgam at that point, which was less electropositive than the sodium, and formed an electric couple with it. If this were so, and if the conditions were made to approximate to those in a voltaic cell, the rate of evolution of hydrogen should become some sort of function of the conductivity of the water or solution.

Further experiments were therefore made, at constant pressure, with a piece of platinum wire in the reaction-vessel which was covered partly by the amalgam and partly by the water.

The results are given in the following table:

Experi- ment.	Time in hours.	c.c. H ₂ . Water alone.	Difference in c.c. H ₂ per hour.	c.c. H ₂ Water + Pt wire.	Difference in c.c. H ₂ per hour.
A	1	1.6	1.6	1.6	1.6
	2	3.4	1.8	4.2	2.6
	3	4.5	1.1	7.3	3.1
	4	5.8	1.3	11.0	3.7
	5	7.5	1.7	16.0	5.0
	6	8.7	1.2	22.2	6.2
	7	10.5	1.8	31.0	8.8
B	1	0.6	0.6	0.9	0.9
	2	1.5	0.9	2.5	1.6
	3	2.3	0.8	4.3	1.8
	4	3.2	0.9	6.6	2.3
	5	4.0	0.8	9.8	3.2
	6	4.8	0.8	13.8	4.0

From this table it will again be observed that the action between the amalgam and water alone proceeds fairly regularly, but, although in the case where the platinum wire is inserted the action proceeds quicker and quicker as time goes on, this acceleration is nothing like so great as the increase which must take place in the conductivity of the solution as the sodium hydroxide accumulates.

In order further to investigate this, the rate of the reaction at the *commencement* was studied by adding various quantities of a dilute solution of pure sodium hydroxide to samples of the water before the amalgam was put in. The conductivities of these solutions were measured.

The sodium hydroxide was prepared by allowing small pieces of sodium to deliquesce on a porcelain funnel under a bell-jar inverted over water, replacing the ordinary air by air freed from carbon dioxide.

Conductivity × 10 ⁻⁶ ...	0.73	0.78	3.45	8.64	9.15	29.8	46.5	117.4
Time in hours.	c.c. H ₂ .	c.c. H ₂ .	c.c. H ₂ .	c.c. H ₂ .	c.c. H ₂ .	c.c. H ₂ .	c.c. H ₂ .	c.c. H ₂ .
1	2.0	0.4	1.6	1.3	1.8	1.4	0.2	0.2
2	5.0	2.2	4.2	3.6	4.5	3.1	2.6	2.6
3	9.2	4.3	8.4	6.3	7.1	5.7	5.7	5.5

It will be seen from this that the addition of sodium hydroxide does not alter in any regular way the rate of commencement of the reaction.

The explanation propounded above, therefore, does not seem to be tenable.

A purer form of amalgam was also prepared by distilling sodium into redistilled mercury in a vacuum. As will be seen from the following table, the reaction was slow, but not of an order differing remarkably from previous reactions.

Time in hours	1.	2.	3.	4.	5.	6.
c.c. H ₂	0.3	1.2	2.0	2.8	3.8	5.0

It appears, therefore, that there is no connexion between the conductivity of the water and the activity of its reaction with sodium amalgam. This being so, the activity of ordinary water must be due to the presence of some impurity which is not eliminated by the ordinary processes employed for the purification of water, and which does not when present in water appreciably affect its electrical conductivity. The only impurity satisfying these conditions would seem to be hydrogen peroxide.

To test this, comparison was made of the activity of our purified water (1) alone, and (2) with the same water to 50 c.c. of which had been added 1 drop of a 1 per cent. solution of distilled hydrogen peroxide.

Time in hours.	c.c. H ₂ from water alone.	c.c. H ₂ from water with H ₂ O ₂ .
$\frac{1}{2}$	unmeasurable	0·6
1	"	3·8
$1\frac{1}{2}$	1·3	10·2
2	2·2	17·6
3	4·1	32·4

Even at this state of dilution (about 1 in 100,000) the hydrogen peroxide therefore has increased the activity enormously.

The conductivity of the water was not appreciably altered by this small quantity of hydrogen peroxide.

Although the amount of hydrogen peroxide added was sufficient to give a very strong colour with titanium oxysulphate before the reaction was started, the solution at the end of the experiment did not show a trace of colour with this reagent.

Apparently the hydrogen peroxide possessed potential powers of starting the reaction, but was then reduced by the nascent hydrogen.

It was then thought possible that the differing activities of different samples of water might be due to the presence of varying quantities of hydrogen peroxide. Hydrogen peroxide, being volatile in steam, would pass over in an ordinary distillation, but would be decomposed if the vapour were heated to redness. Tap-water, the most active of the specimens tried, was found to give no visible colour with titanium oxysulphate; but when potassium iodide and starch, with a trace of ferrous sulphate, were used, a strong blue colour developed. Not even this very delicate test showed any colour, however, either with water distilled from a copper vessel or the special water.

Fifty c.c. of water were then synthesised by passing pure hydrogen and oxygen, obtained from the electrolysis of baryta water, over palladium.

This water was found to act rapidly on sodium amalgam:

Time in hours	1.	2.	3.
c.c. H ₂	6·5	17·4	24·7

Traube has shown (*Ber.*, 1893, **26**, 1471) that palladium-hydrogen, in the presence of oxygen and water, yields hydrogen peroxide. The next point to be proved was whether the test given above by tap-water was due to hydrogen peroxide or to some other oxidising agent.

Tap-water was distilled from a Jena-glass boiler, to which was sealed a Jena-glass condenser.

The middle fraction gave no colour by the potassium iodide and ferrous sulphate test, but the residue in the boiler gave a strong reaction. On distilling tap-water, however, under the same conditions, but having in addition a few pieces of platinum wire or a little finely-divided pure silver in the boiler, neither the distillate nor the residue gave the test, the hydrogen peroxide, if present, having been decomposed by these metals. It was then thought to be of interest to compare the respective activities of these various samples, in relation to their possible content of hydrogen peroxide.

Time in hours.	A. c.c. H ₂ .	B. c.c. H ₂ .	C. c.c. H ₂ .	D. c.c. H ₂ .	E. c.c. H ₂ .
1	18.5	4.7	5.8	4.6	6.7
2	23.9	9.6	13.3	11.5	15.2
3	34.8	14.8	19.8	17.4	22.6
4	—	21.8	26.9	23.4	30.8

(A) Tap-water. Gave a strong colour with potassium iodide, ferrous sulphate, and starch.

(B) Tap-water distilled from Jena-glass apparatus, with pieces of platinum wire in the boiler. Neither the distillate nor the residue gave the above test.

(C) Repetition of (B), using silver instead of platinum. Neither the distillate nor the residue gave the test.

(D) Tap-water alone distilled from Jena-glass vessel. The distillate did not give the test, but the residue in the boiler did.

(E) Residue from (D) distilled almost to dryness. The distillate now gave the test, but not so strong as for tap-water.

The explanation for the activity of water on sodium amalgam seems therefore to be found in the presence of traces of hydrogen peroxide.

Addition of hydrogen peroxide has been shown above to increase the activity enormously, and where the colour tests have shown the presence of hydrogen peroxide, that specimen of water has been shown to be more active than where the test has not been delicate enough to detect it.

All the very inactive specimens of water have been prepared under conditions which would favour the decomposition of hydrogen peroxide; for example, the superheating of the steam in the copper condenser, and the distillation from a platinum

apparatus, again superheating the steam. One distillation by means of the latter method gave the most striking result yet attained, shown in the following table:

Time in hours ...	1.	2.	3.	4.	5.	6.
c.c. H ₂	unmeasurable	unmeasurable	unmeasurable	0·1	0·4	0·5

The explanation propounded above would also account for the fact that the activity of the water is no function of its conductivity, it having been shown above that the addition of a small quantity of hydrogen peroxide to a sample of water, whilst increasing its activity very much, did not appreciably alter its conductivity.

On this explanation, specimens *B*, *C*, and *D* above, whilst not containing enough hydrogen peroxide to give the colour reaction, yet contained enough to give a considerable, and about an equal, velocity to their reaction on sodium amalgam.

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CCXIX.—*The Action of Variously Treated Waters on Sodium Amalgam.*

By LESLIE HENRY PARKER.

WITH reference to the preceding paper by Baker and Parker (p. 2060) on the interaction of sodium amalgam and water, the author has investigated the effect on the activity of water subjected to various treatment. Different metals were sealed up in Jena-glass flasks with about 200 c.c. of the inactive water for periods varying from ten to thirty days, and their effect on the activity of the water was noted. The metals were as pure specimens as possible, and were cleaned with dilute nitric acid, washed about twenty to twenty-five times with distilled water, and steamed in the flasks into which they were to be introduced whilst the former were being cleaned.

In each case a specimen of the water alone was laid aside under similar conditions to act as a comparison.

Time in in hours.	Water alone, sealed <i>cold</i> in flask, 22 days.	Water sealed <i>cold</i> with electrolytic Cu, 12 days.	Water sealed <i>cold</i> with pure Ag, 22 days.	Water sealed <i>cold</i> with Pt, 17 days.
1	0·2 c.c. H ₂	1·7	0·9	3·2
2	0·7	3·1	1·7	5·7
3	1·3	3·5	2·8	6·8
4	1·8	4·0	3·7	7·8
5	2·5	4·2	4·7	8·8
6	3·0	—	5·6	9·4

In the case of the water exposed to copper, the metal was tarnished on the surface, especially where resting against the vessel. The water gave an appreciable colour test for copper on passing hydrogen sulphide.

Time in hours.	Water alone, sealed boiling, 28 days.	Water sealed boiling with Cu, 22 days.	Water sealed boiling with Hg, 19 days.	Water sealed boiling with Al, 20 days.	Water sealed boiling with Al + Ag, 17 days.
1	unmeasurable	1.1	0.7	2.3	3.0
2	0.3 c.c. H ₂	1.7	1.8	4.4	6.2
3	0.5	2.6	3.3	6.0	8.8
4	1.2	3.4	4.7	8.5	11.8
5	1.5	4.3	—	11.5	13.7
6	2.2	5.5	8.0	15.4	16.3

Time in hours.	Water alone, sealed boiling, 21 days.	Water sealed boiling with Cu, 25 days.	Water sealed boiling with heated Ag, 24 days.
1	unmeasurable	0.9	2.8
2	0.5 c.c. H ₂	2.8	7.5
3	1.3	4.9	12.3
4	2.3	7.1	18.1
5	3.6	9.7	—
6	5.0	12.4	—

Time in hours.	Water alone, sealed boiling, 28 days.	Water sealed boiling with Cu, 27 days.	Water sealed boiling with Hg, 19 days.	Water sealed boiling with Al, 29 days.
1	unmeasurable	unmeasurable	0.5	2.3
2	0.9 c.c. H ₂	1.4	2.3	6.7
3	2.1	2.7	—	11.4
4	3.6	4.0	5.5	16.5
5	5.2	5.2	7.3	21.7
6	7.2	6.1	—	—

Time in hours.	Water sealed boiling, 34 days.	Water sealed boiling with Cu, 33 days.	Water sealed boiling with Al, 36 days.
1	1.7 c.c. H ₂	1.4	5.1
2	3.9	3.2	12.7
3	5.5	4.4	21.9
4	7.2	6.1	—
5	8.5	7.4	—

From these figures the general impression is that exposure to metals increases to some extent the activity of the water, more especially in the case of aluminium, whilst copper and mercury have not so much effect.

The explanation of this might be found in assuming the formation of a small amount of hydrogen peroxide during the long standing of the metals with the water and the oxygen dissolved in it.

If this is the case, however, hydrogen peroxide is not formed in sufficient quantity to give the test with potassium iodide, starch, and ferrous sulphate. With the more easily oxidisable metal

aluminium one would expect more hydrogen peroxide to be formed than with copper or mercury. This view is in harmony with the fact which Traube discovered (*Ber.*, 1882, **15**, 670), that considerable quantities of hydrogen peroxide were produced when zinc acted upon water in presence of oxygen, whilst he did not detect it when copper was treated in a similar manner.

However, it has been shown in the preceding paper that a trace of hydrogen peroxide is sufficient to increase the activity enormously, and thus it is quite reasonable to suppose that the quantity of hydrogen peroxide necessary to produce a small increase in the activity would be quite undetectable by the ordinary colour tests.

Further specimens of water were exposed to radium bromide for various periods. The results were certainly interesting.

Time in hours.....	1.	2.	3.	4.	5.	6.
Water alone, sealed <i>cold</i> , 22 days	0.2 c.c. H ₂	0.7	1.3	1.8	2.5	—
Same exposed to RaBr ₂ (closed tube), 28 days...	1.2	2.7	4.3	6.3	8.7	11.0
Water sealed <i>boiling</i> , 28 days	unmeasurable	0.4	0.5	1.2	1.5	—
Same exposed to RaBr ₂ (open tube), 29 days...	2.4	7.2	12.7	18.6	25.0	28.0
Water sealed <i>boiling</i> , 50 days	0.2	1.1	2.4	3.5	4.6	6.0
Same exposed to RaBr ₂ , 50 days	2.9	8.3	14.0	20.0	25.5	—
Water sealed <i>cold</i> , 27 days.....	3.2	6.1	9.2	12.0	15.2	—
Same exposed to RaBr ₂ (closed tube), 35 days...	17.6	38.1	—	—	—	—

Exposure to radium bromide in every case has increased the activity considerably.

In support of the explanation of the varying activities of different samples of water advanced in the previous paper, namely, that hydrogen peroxide is the agent which influences the rate of interaction of sodium amalgam and water, Kailan (*Monatsh.*, 1912, **33**, 1329) has shown that water exposed to the penetrating radiations from radium bromide, in acid, neutral, or alkaline solutions, is partly transformed into hydrogen peroxide.

This would account for the increase of activity of the water so exposed, and the explanation put forward above would seem to be the only one consistent with all the observed facts.

CCXX.—*Studies in the Diphenyl Series. Part V.*
Derivatives and Substitution Products of the Two
Isomeric o-Dinitrobenzidines and Synthesis of
Derivatives of Benzerythrene.

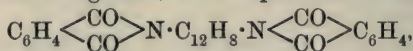
By JOHN CANNELL CAIN, ALBERT COULTHARD, and
 FRANCES MARY GORE MICKLETHWAIT.

IN Part II of this series (T., 1912, **101**, 2298) proof was adduced of the existence of two different *o*-dinitrobenzidines, and it was also shown that these yield two different acetyl derivatives, and, by elimination of the amino-groups, two different dinitrodiphenyls.

In order further to study the difference between these bases, several derivatives have been prepared from each (*di*formyl, *dibenzoyl*, and *disuccinyl*), each pair proving to be different.

In addition, a study of the action of phthalic anhydride and of its di- and tetra-chloro-derivatives on the two dinitrobenzidines led to results which may help to throw light on the constitution of these bases. It has been shown by Koller (*Ber.*, 1904, **37**, 2880) that when benzidine and phthalic anhydride are boiled together in aqueous suspension, the cyclic compound, phthalylbenzidine, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{NH} \cdot C_6H_4 \\ \text{CO} \cdot \text{NH} \cdot C_6H_4 \end{smallmatrix}$, is formed, and the unimolecular

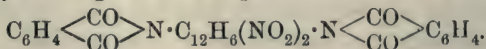
character of such compounds has been proved by Kaufler (*Annalen*, 1907, **351**, 151; *Ber.*, 1907, **40**, 3250). When, however, the above materials are heated together, 4:4'-diphthaliminodiphenyl,



is formed (Bandrowski, *Ber.*, 1884, **17**, 1181). On applying these two reactions to the two dinitrobenzidines, the 3:3'-isomeride furnished, in both cases, the cyclic compound, 3:3'-*dinitrophthalyl-*

benzidine, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{NH} \cdot C_6H_3 \cdot \text{NO}_2 \\ \text{CO} \cdot \text{NH} \cdot C_6H_3 \cdot \text{NO}_2 \end{smallmatrix}$, whilst the 3:5'-isomeride did

not react at all in aqueous suspension, and, when heated with phthalic anhydride, gave 4:4'-*diphthalimino-3:5'-dinitrodiphenyl*,



It would thus appear that under these conditions 3:3'-dinitrobenzidine exhibits much more tendency to form a cyclic compound with phthalic anhydride than does the 3:5'-isomeride, and it may be that, when further results have been accumulated, Kaufler's stereochemical formula for benzidine (*Annalen*, *loc. cit.*) will be

of help in deciding the influence of the nitro-groups in these reactions.

With 3:6-dichlorophthalic anhydride both bases gave the corresponding dichlorophthalimino-derivative, whilst with 3:4:5:6-tetrachlorophthalic anhydride the cyclic phthalyl compounds were produced.

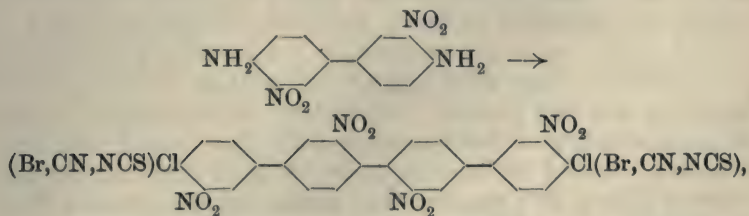
Besides the above compounds, certain bisazo-derivatives of each base have been prepared by the aid of phenol, β -naphthol, 1-naphthylamine-4-sulphonic acid (naphthionic acid) and 8-amino-1-naphthol-3:6-disulphonic acid (H-acid), the corresponding pairs of bisazo-compounds being found to be markedly different in each case.

Further, each base has been submitted to the diazo-reaction with the object of replacing the amino-groups by chlorine, bromine, iodine, hydroxyl, cyanogen, and the thiocyanogroup.

Through this reaction the two *o*-dinitrobenzidines have been found to exhibit a still greater difference in their chemical behaviour than was disclosed by the reactions studied in the former paper (*loc. cit.*). In carrying out the replacement of the amino-groups by chlorine, bromine, and cyanogen, by means of copper bronze (Ullmann's method), and by the thiocyanogroup (without the use of copper), 3:3'-dinitrobenzidine gave the expected substitution products (except in the case of bromine, see p. 2081), but 3:5'-dinitrobenzidine showed an entirely different behaviour. Instead of the expected substitution products, it was found that two diphenyl nuclei coalesced, with the production of derivatives of benzerythrene:

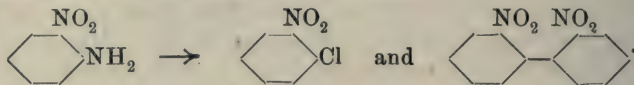


So far as we know, the compounds described in this paper are the first substitution products of this hydrocarbon that have been obtained, and their formation, represented thus:



is paralleled in an interesting manner in the case of *o*-nitroaniline, which, under similar conditions (using either copper powder or cuprous chloride), yields a mixture of *o*-chloronitrobenzene and

2: 2'-dinitrodiphenyl (Niementowski, *Ber.*, 1901, **36**, 3325; Ullmann and Forgan, *ibid.*, 3803), thus:



In the replacement of the amino-group by iodine (where no copper was used), the reaction followed the normal course, the two di-iododinitro-derivatives differing from each other.

Some ten years ago, during an investigation of the action of water on dianisidine and 3: 3'-dichlorobenzidine, bases containing acidic groups in the ortho-position with respect to the amino-groups (Cain, T., 1903, **83**, 688), it was found that the chief product in each case was a dark-coloured insoluble substance, to which a quinonoid constitution was assigned, and that only in the case of 3: 3'-dichlorobenzidine was it possible to isolate a trace of 3: 3'-dichloro-*p*-diphenol. It was to be anticipated, therefore, that on applying this reaction to the case of the *o*-dinitrobenzidines containing strongly acidic groups in the ortho-position to the amino-groups, difficulties might be experienced in substituting the amino-groups by hydroxyl. By carrying out the reaction in the ordinary manner, namely, by heating the bisdiazonium salts of the two dinitrobenzidines with water or dilute sulphuric acid, only traces of phenolic substances were formed, but by a variation of this method three different substances, all of the composition of the corresponding dinitrodiphenol, were obtained from 3: 3'-dinitrobenzidine, and one dinitrodiphenol, apparently different from any of the above, was produced from 3: 5'-dinitrobenzidine. All these dinitrodiphenols appear to be of high molecular weight, as they are brown and amorphous, and do not resemble in any way the dinitrodiphenol obtained by nitrating 4: 4'-diphenol (see below). Since the work on dianisidine and 3: 3'-dichlorobenzidine was carried out, it was shown by Orton, Coates, and Burdett (T., 1907, **91**, 35) that in many cases (in the benzene series) where this reaction was difficult or impossible to bring about, the substitution could be effected easily by means of sunlight. Accordingly, solutions of the diazotised bases were exposed to sunlight until no more diazonium salt was present. Incidentally this experiment showed the great stability of the diazonium salts; that from 3: 3'-dinitrobenzidine, exposed to light in June, 1913, at the ordinary temperature (about 20°) required two weeks, and that from 3: 5'-dinitrobenzidine, about three weeks, before the decomposition was at an end. The experiments were successful in so far as hydroxy-compounds were produced; in fact, two different hydroxy-compounds were isolated from each base, but from neither base

was there obtained a dinitrodiphenol identical with that described by Kunze (*Ber.*, 1888, **21**, 3331; compare also Schütz, *ibid.*, p. 3530), namely:



prepared by nitrating 4:4'-diphenol, or that discovered by Goldstein (*J. Russ. Phys. Chem. Soc.*, 1874, **6**, 193; 1878, **10**, 318) by oxidising *o*-nitrophenol, the constitution of which is not known.* From each base was obtained a compound having the composition of a dinitro-4:4'-diphenol and one having the composition of a tetranitrodihydroxybenzerythrene, the latter evidently having been produced by the coalescence of two diphenyl nuclei as in the case of the experiments mentioned above; they were easily separated by means of alcohol, but only one of the four compounds melted below 300°.

EXPERIMENTAL.

I.—Derivatives of 3:3'- and 3:5'-Dinitrobenzidine.

3:3'-Dinitrodiformylbenzidine, prepared by heating the base with anhydrous formic acid, is very soluble in nitrobenzene, and separates from acetic acid in brownish-yellow crystals, melting at 188°:

0.2596 gave 38 c.c. N₂ at 21° and 761 mm. N=17.09.

C₁₄H₁₀O₆N₄ requires N=16.97 per cent.

3:5'-Dinitrodiformylbenzidine separates from nitrobenzene in golden-yellow crystals, melting and decomposing at 282°:

0.1054 gave 15.2 c.c. N₂ at 19° and 759 mm. N=16.97.

C₁₄H₁₀O₆N₄ requires N=16.97 per cent.

A mixture of the above two compounds melted at 260°.

Dibenzoyl-3:3'-dinitrobenzidine, prepared by heating the base with benzoyl chloride, separates from nitrobenzene in yellow crystals, melting at 290°:

0.2719 gave 26.6 c.c. N₂ at 17° and 761 mm. N=11.63.

C₂₆H₁₈O₆N₄ requires N=11.62 per cent.

Dibenzoyl-3:5'-dinitrobenzidine crystallises from nitrobenzene in golden-yellow needles, melting at 298°:

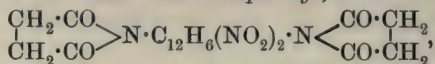
0.1691 gave 17 c.c. N₂ at 21° and 760 mm. N=11.77.

C₂₆H₁₈O₆N₄ requires N=11.62 per cent.

A mixture of the above two compounds melted at 270°.

* Experiments are in progress with the object of elucidating the constitution of this compound.

3: 3'-Dinitro-4: 4'-disucciniminodiphenyl,



was prepared by heating 3: 3'-dinitrobenzidine with succinic anhydride at 150—160° for six hours. The alcoholic extract of the product furnished bright yellow crystals, melting at 203°:

0·0824 gave 9·1 c.c. N₂ at 18° and 763 mm. N=13·00.

C₂₀H₁₄O₈N₄ requires N=12·78 per cent.

3: 5'-Dinitro-4: 4'-disucciniminodiphenyl, prepared similarly at 140°, is insoluble in alcohol or benzene, but separates from nitrobenzene in yellow crystals, melting at 238°:

0·1016 gave 11·1 c.c. N₂ at 15° and 760 mm. N=12·93.

C₂₀H₁₄O₈N₄ requires N=12·78 per cent.

3: 3'-Dinitrophthalylbenzidine, C₆H₄ < $\begin{array}{c} \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_3 \cdot \text{NO}_2 \\ \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_3 \cdot \text{NO}_2 \end{array}$ — This

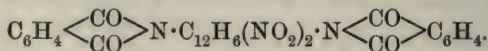
compound is formed when molecular proportions of phthalic anhydride and 3: 3'-dinitrobenzidine are boiled in aqueous suspension for seven to eight hours. The orange-yellow product was crystallised first from dilute alcohol, and then from nitrobenzene, when it melted at 297—298°:

0·1124 gave 13·4 c.c. N₂ at 21° and 767 mm. N=13·96.

C₂₀H₁₂O₆N₄ requires N=13·86 per cent.

The substance is also formed when 3: 3'-dinitrobenzidine and phthalic anhydride (2 mols.) are heated together at 140—150° for four hours (Found, N=14·00. Calc., N=13·86 per cent.).

4: 4'-Dipthalimino-3: 5'-dinitrodiphenyl,*



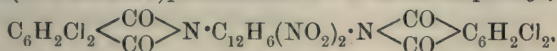
—When 3: 5'-dinitrobenzidine was boiled in aqueous suspension with phthalic anhydride, no action took place even after two days, but on heating the materials at 140—150° for four hours, interaction occurred. The product was crystallised from nitrobenzene, and was found to consist of a mixture of a greyish-yellow substance (m. p. 265°), of which the amount formed was not sufficient for analysis, and canary-yellow crystals; the latter, which did not melt at 305°, were specifically lighter than the former, and mechanical separation was effected by means of benzene:

0·1582 gave 14·7 c.c. N₂ at 22° and 761 mm. N=10·78.

C₂₈H₁₄O₈N₄ requires N=10·48 per cent.

* The corresponding compound from 3: 3'-dinitrobenzidine, which was analysed by Bandrowski (*Monatsh.*, 1887, 8, 472), separates from nitrobenzene in pale yellow crystals melting at 284°; Bandrowski did not give the melting point.

4: 4'-Di(3:6-dichloro)phthalimino-3: 3'-dinitrodiphenyl,



was prepared by heating a mixture of 3:6-dichlorophthalic anhydride and 3: 3'-dinitrobenzidine at 100—135° for four to five hours. The product was extracted with alcohol, and the greyish-yellow residue, which was soluble in benzene, melted at 191—192°:

0.1103 gave 8.1 c.c. N_2 at 19° and 760 mm. $\text{N}=8.58$.

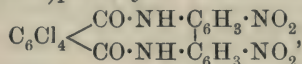
$\text{C}_{28}\text{H}_{12}\text{O}_8\text{N}_4\text{Cl}_4$ requires $\text{N}=8.30$ per cent.

4: 4'-Di(3:6-dichloro)phthalimino-3: 5'-dinitrodiphenyl was prepared by heating a mixture of 3:6-dichlorophthalic anhydride and 3: 5'-dinitrobenzidine at 150—160° for four hours. The product was extracted with alcohol, and the residue dissolved in benzene; on adding alcohol to the solution, a gelatinous, pale grey substance separated, which melted at 205° after turning yellow and shrinking at about 184°:

0.1377 gave 10.0 c.c. N_2 at 17.5° and 763 mm. $\text{N}=8.56$.

$\text{C}_{28}\text{H}_{12}\text{O}_8\text{N}_4\text{Cl}_4$ requires $\text{N}=8.30$ per cent.

(3:4:5:6-Tetrachloro)phthalyl-3: 3'-dinitrobenzidine,



was obtained by heating 3: 3'-dinitrobenzidine with tetrachlorophthalic anhydride (2 mols.) at 100—130° for four hours. The product, after extraction with alcohol and then with benzene, separated from nitrobenzene in yellow crystals, melting at 312°:

0.1798 gave 16.5 c.c. N_2 at 20° and 760 mm. $\text{N}=10.69$.

$\text{C}_{20}\text{H}_8\text{O}_6\text{N}_4\text{Cl}_4$ requires $\text{N}=10.33$ per cent.

(3:4:5:6-Tetrachloro)phthalyl-3: 5'-dinitrobenzidine, similarly prepared from 3: 5'-dinitrobenzidine, crystallises in pale yellow needles, which do not melt at 310°:

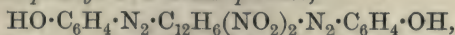
0.2211 gave 19.8 c.c. N_2 at 24° and 767 mm. $\text{N}=10.40$.

$\text{C}_{20}\text{H}_8\text{O}_6\text{N}_4\text{Cl}_4$ requires $\text{N}=10.33$ per cent.

A mixture of this and the preceding compound melted at 270°.

Azo-derivatives.

3:3'-Dinitrodiphenyl-4:4'-bisazophenol,*



prepared by adding a diazotised solution of the base to an alkaline solution of phenol, separates from xylene as a reddish-brown powder melting at 240—245°.

* Estimations of nitrogen in this and the three following compounds gave results from 0.6 to 1.8 below the calculated percentage, evidently due to the extreme difficulty in burning them.

3:5'-Dinitrodiphenyl-4:4'-bisazophenol, $C_{24}H_{16}O_6N_6$, separates from acetic acid as a black, amorphous powder, melting and decomposing at 250—255°.

3:3'-Dinitrodiphenyl-4:4'-bisazo- β -naphthol, $C_{32}H_{20}O_6N_6$, is a bright red powder insoluble in the usual organic solvents. It melts and decomposes at about 297° with previous sintering.

3:5'-Dinitrodiphenyl-4:4'-bisazo- β -naphthol is a black powder, very sparingly soluble in xylene, which does not melt at 335°. The diazotised bases were also combined with 1-naphthylamine-4-sulphonic acid (naphthionic acid) and with 8-amino-1-naphthol-3:6-disulphonic acid (H-acid) in order to obtain soluble bisazo-colouring matters, the shades of which on cotton could be compared.

The colouring matter from 3:3'-dinitrobenzidine and naphthionic acid dyes cotton in reddish-violet shades resembling those produced by "Congo Corinth B," whilst the corresponding colouring matter from 3:5'-dinitrobenzidine produces a bluer shade on cotton, similar to that furnished by "Azo-violet." Both these dyeings are changed to red by mineral acids. With "H-acid," 3:3'-dinitrobenzidine gave a reddish-grey (similar to "Direct Grey B"), whilst 3:5'-dinitrobenzidine gave a greenish-grey.

II.—The Diazo-reaction Applied to the Dinitrobenzidines: *Synthesis of Derivatives of Benzerythrene.*

In these experiments the bases were dissolved in concentrated sulphuric acid, the solutions cooled in ice, diluted slightly with water until the base began to separate, and diazotised by adding sodium nitrite. The solution was then filtered, and treated in the usual way.

Chlorine.—The diazo-solution was poured on copper bronze and hydrochloric acid.

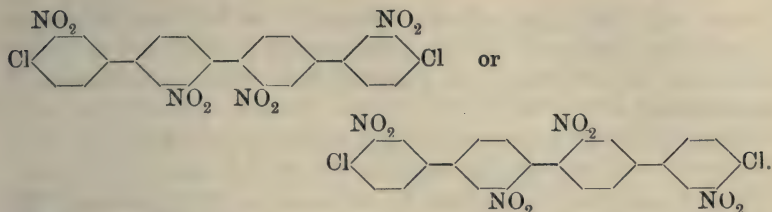
From 3:3'-dinitrobenzidine there was obtained 4:4'-dichloro-3:3'-dinitrodiphenyl, which crystallises from glacial acetic acid in pale yellow needles melting at 111—112°:

0.1011 gave 7.7 c.c. N_2 at 18.5° and 764.3 mm. $N=8.9$.

$C_{12}H_6O_4N_2Cl_2$ requires $N=8.9$ per cent.

3:5'-Dinitrobenzidine, when similarly treated, gave 4'':4'''-dichlorotetranitrobenzerythrene*:

* The ring system of benzerythrene has not yet been numbered. In Richter's "Lexikon" the name "4:4'-diphenylbiphenyl" is assigned to it. Neither this name nor "*p*-bisdiphenyl" appears to be suitable when substitution



which is soluble in benzene or glacial acetic acid, but insoluble in light petroleum or alcohol, and forms yellow crystals melting at 203° :

0.1082 gave 9.4 c.c. N_2 at 20° and 765 mm. $N=10.2$.

$C_{24}H_{12}O_8N_4Cl_2$ requires $N=10.1$ per cent.

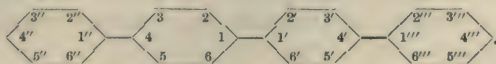
In various preparations of this substance it was obvious that an azo-compound was simultaneously formed, as the values obtained in the estimation of nitrogen were often considerably higher than required by the above formula.

Bromine.—The products obtained in various experiments by treating the diazotised solution of 3:3'-dinitrobenzidine with hydrobromic acid and copper bronze or cuprous bromide all contained more nitrogen than was required by the expected dibromodinitrodiphenyl, or even by the corresponding derivative of benzerythrene, and evidently this was due to the presence of some azo-compound. 4:4'-Dibromo-3:3'-dinitrodiphenyl was, however, easily prepared by treating the diazotised solution with hydrobromic acid and bromine, and decomposing the perbromide formed in this way with glacial acetic acid (Saunders, *Amer. Chem. J.*, 1891, **13**, 486). It separates from glacial acetic acid in orange crystals melting at 137 — 138° :

0.1418 gave 8.6 c.c. N_2 at 23° and 765 mm. $N=7.0$.

$C_{12}H_6O_4N_2Br_2$ requires $N=7.0$ per cent.

The diazotised solution from 3:5'-dinitrobenzidine, when partly neutralised with sodium hydroxide and then treated with hydro-products are concerned. We therefore prefer to use "benzerythrene" and number the carbon atoms thus:



Further, in the absence of any direct chemical evidence (except as to the ortho-position of the nitro-groups) we have been compelled to refer to the two bases as 3:3'- and 3:5'-dinitrobenzidine (T., 1912, **101**, 2301; compare also this vol., p. 591). This being so we do not feel justified in assuming these positions in the benzerythrene compounds, as an additional complication is introduced as indicated in the two formulæ given.

bromic acid and copper powder, yielded 4'' : 4'''-dibromotetranitrobenzerythrene, which is soluble in benzene or alcohol, and separates from the latter solvent in greyish-yellow crystals melting and decomposing at 184°:

0.1218 gave 9.4 c.c. N₂ at 30° and 762 mm. N=8.7.

C₂₄H₁₂O₈N₄Br₂ requires N=8.7 per cent.

This formula was confirmed by an estimation of bromine. By treating the diazotised solution of 3:5'-dinitrobenzidine with hydrobromic acid and bromine, and decomposing the perbromide formed with glacial acetic acid, 4:4'-dibromo-3:5'-dinitrodiphenyl was obtained. This separates from glacial acetic acid in orange-yellow crystals melting at 247°:

0.1603 gave 9.7 c.c. N₂ at 20° and 759 mm. N=7.0.

C₁₂H₆O₄N₂Br₂ requires N=7.0 per cent.

Cyanogen.—The diazotised solution prepared from 3:3'-dinitrobenzidine was partly neutralised with sodium hydroxide, and treated in the usual manner with cuprous cyanide. 3:3'-Dinitro-4:4'-dicyanodiphenyl, which was extracted from the product by means of benzene, separates from this solvent as a brown powder melting and decomposing at 190—192°:

0.1322 gave 22.2 c.c. N₂ at 29° and 762 mm. N=19.0.

C₁₄H₆O₄N₄ requires N=19.0 per cent.

This nitrile, when hydrolysed, furnishes an acid, which, however, could not be obtained in a pure state.

3:5'-Dinitrobenzidine, when similarly treated, gave 4'' : 4'''-dicyanotetranitrobenzerythrene, which is insoluble in ether, benzene, or alcohol, but dissolves in glacial acetic acid, and separates, on diluting the solution with water, as an amorphous, yellow powder, melting and decomposing at 195—198°:

0.0944 gave 12.5 c.c. N₂ at 22° and 767.2 mm. N=15.5.

C₂₆H₁₂O₈N₆ requires N=15.7 per cent.

Hydrolysis of this nitrile furnished an acid, which could not be obtained in a pure state.

Iodine.—3:3'-Dinitrobenzidine gave, on diazotisation and treatment of the solution with potassium iodide, 4:4'-di-iodo-3:3'-dinitrodiphenyl, which crystallises from dilute alcohol in yellow needles melting at 151—152°:

0.2342 gave 11.45 c.c. N₂ at 11° and 754.6 mm. N=5.8.

C₁₂H₆O₄N₂I₂ requires N=5.6 per cent.

3:5'-Dinitrobenzidine gave 4:4'-di-iodo-3:5'-dinitrodiphenyl, which is soluble in glacial acetic acid, alcohol, or xylene, but insoluble in acetone or benzene, and forms yellow crystals melting at 252—253°:

0.2010 gave 10.7 c.c. N_2 at 24° and 762 mm. $N=6.1$.

$C_{12}H_6O_4N_2I_2$ requires $N=5.6$ per cent.

Thiocyano-group.—The diazotised solution prepared from 3:3'-dinitrobenzidine was treated with sodium acetate until little mineral acid was present, and then poured into aqueous potassium thiocyanate. The 3:3'-dinitro-4:4'-dithiocyanodiphenyl separated from alcohol in very pale, brick-red crystals, melting at 158° :

0.1028 gave 13.5 c.c. N_2 at 15° and 768 mm. $N=15.74$.

$C_{14}H_6O_4N_4S_2$ requires $N=15.64$ per cent.

3:5'-Dinitrobenzidine, when treated in the same way, gave tetranitro-4'':4'''-dithiocyanobenzerhythrene, which separates from nitrobenzene as a yellow powder decomposing at 301° :

0.1668 gave 19.7 c.c. N_2 at 18° and 770 mm. $N=14.04$.

$C_{26}H_{12}O_8N_6S_2$ requires $N=14.00$ per cent.

Hydroxyl.—When the two dinitrobenzidines are diazotised and the solutions boiled, minute amounts of phenolic substances are formed, the main products being brown, amorphous, insoluble substances. By adding the diazotised solution from 3:3'-dinitrobenzidine to a boiling mixture of a solution of sodium sulphate and sulphuric acid (Eng. Pat. 7233 of 1897), a yellowish-brown, amorphous substance was obtained, which was soluble in sodium hydroxide. A portion of this dissolved in alcohol, but did not melt below 300° . Analysis indicated that the substance had the composition of a 3:3'-dinitro-4:4'-diphenol, but its amorphous and infusible condition indicates that it possesses a higher molecular weight than that calculated from the simple formula:

0.1523 gave 13.7 c.c. N_2 at 22° and 757 mm. $N=10.38$.

$(C_{12}H_8O_6N_2)_x$ requires $N=10.14$ per cent.

The alcoholic filtrate from the above, on evaporation, yielded a brown, amorphous substance melting at 105° , which had the composition of a 3:3'-dinitro-4:4'-diphenol combined with water:

0.3055 gave 24.0 c.c. N_2 at 17° and 761 mm. $N=9.26$.

0.2574 lost 0.0170 at $110-120^\circ$. $H_2O=6.19$.

$C_{12}H_8O_6N_2 \cdot H_2O$ requires $N=9.52$; $H_2O=6.12$ per cent.

The anhydrous substance decomposed at $200-205^\circ$.

The part of the above-mentioned yellowish-brown substance which did not dissolve in alcohol (or glacial acetic acid) did not melt at 310° :

0.1646 gave 14.35 c.c. N_2 at 23° and 761 mm. $N=10.08$.

$(C_{12}H_8O_6N_2)_x$ requires $N=10.14$ per cent.

This substance has thus the composition of a 3:3'-dinitro-4:4'-diphenol of high molecular weight.

On decomposing the diazo-solution with a boiling solution of copper sulphate (D.R.-P. 167211), the product was only partly soluble in sodium hydroxide; the soluble portion furnished the hydrated compound melting at 105° , described above.

The above reactions were repeated with 3:5'-dinitrobenzidine, and a third reaction, which consisted in adding the diazo-solution to hot concentrated sulphuric acid, was also carried out. From each of the three experiments a very small amount of a substance soluble in sodium hydroxide was obtained, the main product being brown, amorphous, and insoluble. The material soluble in alkali separated from dilute acetic acid as a yellow powder, which was apparently identical with the 3:5'-dinitro-4:4'-diphenol obtained by the action of light on diazotised 3:5'-dinitrobenzidine (see below).

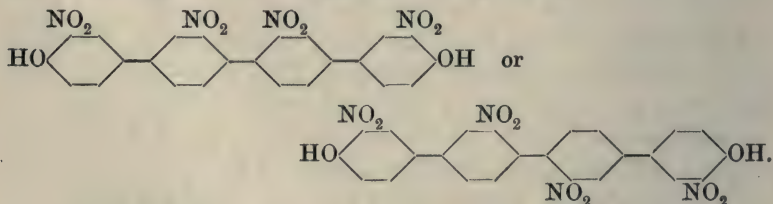
Action of Light on the Diazo-solutions.

The diazotised solutions were submitted to the action of sunlight at the ordinary temperature until decomposition was complete (Orton, Coates, and Burdett, *loc. cit.*). The precipitates formed from each solution were soluble in sodium hydroxide, and were separated by means of alcohol into two portions, one being soluble and the other insoluble in this solvent. In the case of 3:3'-dinitrobenzidine, decomposition was complete in two weeks, and there were obtained a 3:3'-dinitro-4:4'-diphenol, which did not melt at 300° , and was soluble in alcohol:

0.1192 gave 10.4 c.c. N_2 at 23° and 764 mm. $N=10.1$.

$(C_{12}H_8O_6N_2)_x$ requires $N=10.1$ per cent.

and a tetranitro-4'':4'''-dihydroxybenzerythrene,



which did not melt at 330° , and was insoluble in alcohol:

0.2042 gave 19.5 c.c. N_2 at 19° and 763 mm. $N=11.2$.

$C_{24}H_{14}O_{10}N_4$ requires $N=10.8$ per cent.

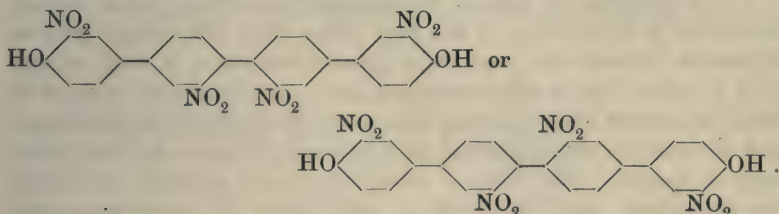
Both the above substances were brown and amorphous.

In the case of 3:5'-dinitrobenzidine, decomposition was complete in three weeks, and there were obtained a 3:5'-dinitro-4:4'-diphenol, which separated from glacial acetic acid or alcohol as a brown, amorphous substance, melting at about 180° :

.01152 gave 10.35 c.c. N_2 at 19.5° and 763 mm. $N=10.5$.

$C_{12}H_8O_6N_2$ requires $N=10.1$ per cent.,

and a *tetranitro-4'' : 4'''-dihydroxybenzerythrene*,



a brown, amorphous substance, which did not melt at 330° , and was insoluble in alcohol:

0.1646 gave 15.35 c.c. N_2 at 25° and 770 mm. $N=10.8$.

$C_{24}H_{14}O_{10}N_4$ requires $N=10.8$ per cent.

Whether this substance was identical or not with that described above could not be ascertained owing to their infusible nature.

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CCXXI.—*Absorption Spectra and Chemical Reactivity.* *Part III. Trinitrobenzene, Trinitroanisole, and Picric Acid.*

By EDWARD CHARLES CYRIL BALY and FRANCIS OWEN RICE.

IN three previous papers (T., 1912, **101**, 1469, 1475; this vol., p. 91) the general theory was put forward that any molecule of a substance in the free state is the centre of a closed field due to the condensing together of the force lines arising from the free affinities of the individual atoms within the molecules. It was shown how these condensed fields may be unlocked or opened by their interpenetration by the force lines arising from the residual affinity of the molecules of a second substance when the two are mixed. By the residual affinity is meant the balance of free affinity after the maximum possible condensation has taken place. Loose systems between the molecules are formed in this way, which

correspond with the solvates formed when substances exist in solution.

In considering the mechanism by which the closed force field of any one molecule is opened by the residual affinity of a second substance, it is evident, in the first place, that there must exist a difference between the two. As a general statement it may be said that in order that a substance may have its closed field opened it must be treated with a second substance, which differs in character, and the greater the difference in character the more will the force field be opened. The point of attack may vary with the nature of the compound, and, of course, in some cases the same compound will be opened both by a strong acid and by a strong base, the nature of the opening being different in the two cases. Such a compound is amphoteric in the real sense of the term, and the correct definition of an amphoteric substance is a compound of such a type that its closed force field is opened differently by an acid and by a base.

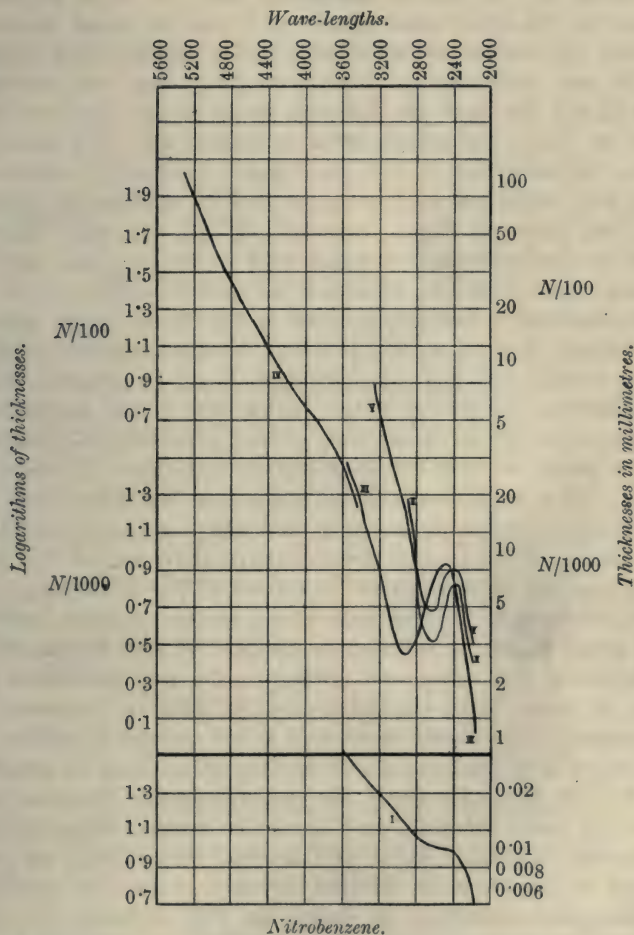
In the second place, it follows from the general conception that the opening up process will be carried out in stages. This was emphasised in a previous paper dealing with the application of the theory to fluorescence (T., 1912, **101**, 1469). Whereas previously only two of the stages had been recognised in the opening up, we have now succeeded in studying the process more completely, and in recognising several distinct stages.

One point of interest at once arises from the existence of the various stages in the opening up of the closed force fields. The evidence of experiment clearly shows that these stages possess a separate and distinct existence, and are stable under the necessary conditions. They represent the same substance with different free energy contents, since the greater the amount of condensation which takes place between the force lines the greater the free energy that escapes. In order, therefore, to convert a substance from stage 1 (in which the maximum possible condensation exists) into stage 2, or first partly opened up condition, a definite quantity of free energy is required. In other words, free substances must necessarily take up energy in definite quanta, a conclusion that is of some importance in relation to Planck's energy quantum theory and photochemistry.

In the present paper we deal with the application of the theory to nitro-derivatives of benzene, and more particularly to trinitrobenzene, picric acid, and trinitroanisole. In previous papers (T., 1905, **87**, 1332; 1910, **97**, 591) it was pointed out that in nitrobenzene the affinities of the nitro-group and phenyl residues mutually influence one another in such a way that only a very small selective absorption is exhibited. It is a well-known fact that

the nitro-group in the aliphatic nitro-compounds and in the metallic nitrates tends to give powerful selective absorption, and the same is true of the phenyl residue in benzene and its homologues. In nitrobenzene, however, the free affinities of the two

FIG. 1.



- I. Pure substance.
 II. In alcohol.
 III. In 80 per cent. sulphuric acid.

- IV. In dimethylaniline.
 V. m-Nitrobenzenesulphonic acid in 80 per cent. sulphuric acid.

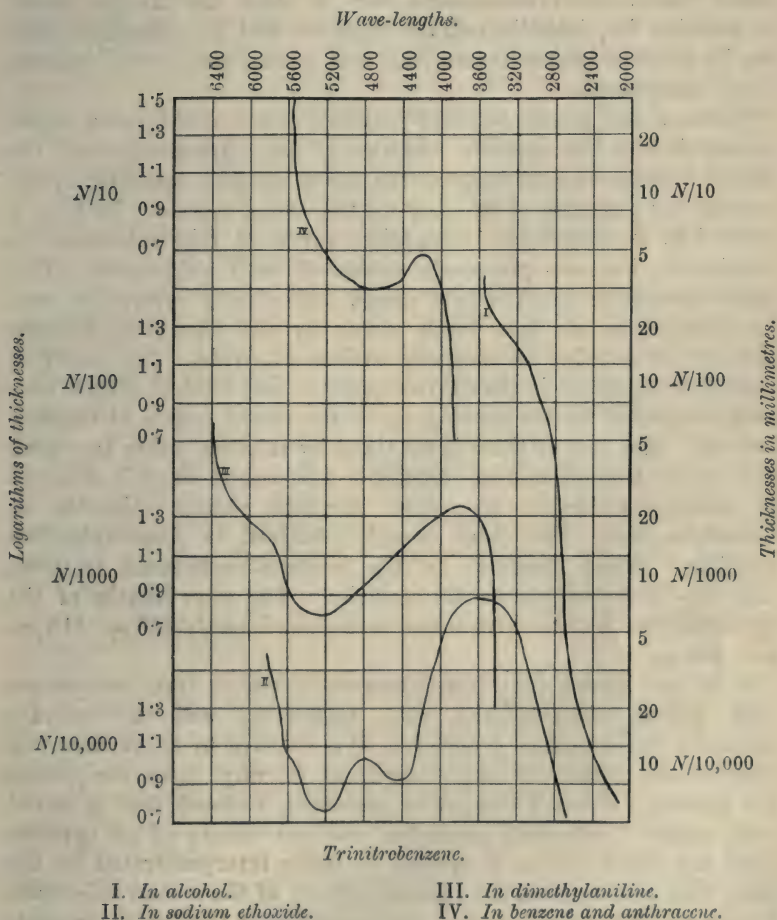
groups have condensed together to give a very stable system, which is not readily opened up by the ordinary solvents in the presence of light. A small absorption band is therefore exhibited by nitrobenzene in the ordinary solvents, which diminishes to a step-out

when the pure liquid is examined. Evidently, therefore, the free affinities of the nitro-group and the phenyl residue are of opposite character, and whilst that of the nitro-group is electronegative or acid in type, that of the phenyl group is of an electropositive or basic type. It is quite possible, however, to open up the system of nitrobenzene by the use of special solvents. It is an amphoteric substance in the strict sense of the word, for the closed system can be opened by solution either in moderately concentrated sulphuric acid (80 per cent.) or in dimethylaniline, and the absorption spectra in the two cases are different owing to the difference in the manner in which the nitrobenzene is opened up. The absorption curves of nitrobenzene in the pure state, in alcoholic solution, in 90 per cent. sulphuric acid solution, and in solution in dimethylaniline, are shown in Fig. 1, curves I, II, III, and IV.* Curve V is that of *m*-nitrobenzenesulphonic acid in 80 per cent. sulphuric acid, and shows from the difference between it and curve III that the nitrobenzene is not sulphonated in the 80 per cent. sulphuric acid solution. The absorption curve of the dimethylaniline solution does not exhibit any definite absorption band, but shows evidences of considerable absorption of the visible rays of the spectrum. It is obvious from these curves that a very profound modification is brought about in the nitrobenzene by solution in these two solvents. It is amphoteric in the sense that its closed force fields is differently attacked by a strong acid and a strong base. As was stated above, owing to the electropositive character of the phenyl nucleus and the electronegative character of the nitro-group, nitrobenzene forms a very completely closed system which is opened to a very small degree by solution in alcohol. If now trinitrobenzene be considered, this compound, owing to the two additional nitro-groups, is much more electronegative or acid in character than nitrobenzene. The closed force field is not opened by alcohol, and the solution in this solvent shows no absorption band at all (Fig. 2, curve I). On the other hand, the closed system is extremely easily opened by basic solvents, and here the results obtained are of considerable interest. As is well known, the addition of sodium ethoxide to the alcoholic solution develops a fine red colour, and the absorption spectrum is shown in Fig. 2, curve II, which gives the absorption curve of a trinitrobenzene in the presence of *N*/10-sodium ethoxide. Almost identical absorption is shown by

* Whereas in all previous papers the absorption curves have been drawn in terms of oscillation frequencies ($1/\lambda$), all the curves in this paper are drawn in terms of wave-lengths. This change has been adopted in response to a direct request from Professor Kayser. Professor Kayser, who is a member of the International Committee on Wave-length Standards, has advised us that the expression of all measurements of absorption in terms of wave-lengths is much to be preferred.

trinitrobenzene in piperidine solution, the difference between the two curves being very slight. In each case two absorption bands are shown, and therefore light vibrations of two frequencies are absorbed under these conditions, and evidently, therefore, two differing amounts of free energy are being absorbed simultane-

FIG. 2.



ously. It follows from this that two different stages in the opening-up process of trinitrobenzene are produced by the action of sodium ethoxide and by piperidine. The absorption of trinitrobenzene in dimethylaniline solution is shown in Fig. 2, curve III, and again there are evidences of two stages in the opening-up of its closed systems. One very marked absorption band is shown, and a

step-out at greater wave-length, which shows that another stage is also brought into play. It is interesting to note that the more refrangible absorption band of the dimethylaniline solution is the same as the less refrangible band of the piperidine solution, so that one stage in the opening-up is common to both solutions. We have therefore altogether three distinct stages in the opening up of the closed system of trinitrobenzene, two of which are brought about by solution in alcoholic sodium ethoxide and in piperidine, and two by solution in dimethylaniline, and middle stage being common to all the solvents.

The fact that trinitrobenzene possesses such a well-marked closed system due to the opposite affinities of the nitro-groups and the phenyl residue, at once suggests the use of complex aromatic hydrocarbons for purposes of opening up the closed system. In Fig. 2, curve IV, is shown the absorption curve of trinitrobenzene in solution in benzene previously saturated with anthracene. One broad absorption band is here shown, and clearly covers the same wave-lengths as the two bands shown by the piperidine solution and by the solution in alcoholic sodium ethoxide. The result of these investigations is that three separate and distinct stages have been recognised in the opening up of the closed system of trinitrobenzene. The first of these is obtained by solution either in piperidine or in alcoholic sodium ethoxide. The second stage is obtained by solution either in piperidine, alcoholic sodium ethoxide, or dimethylaniline. The third is only obtained in dimethylaniline solutions. When dissolved in the benzene-anthracene mixture, both the first two phases also co-exist. The wave-lengths of the light absorbed by the three stages are approximately $430\ \mu\mu$, $515\ \mu\mu$, and $600\ \mu\mu$.

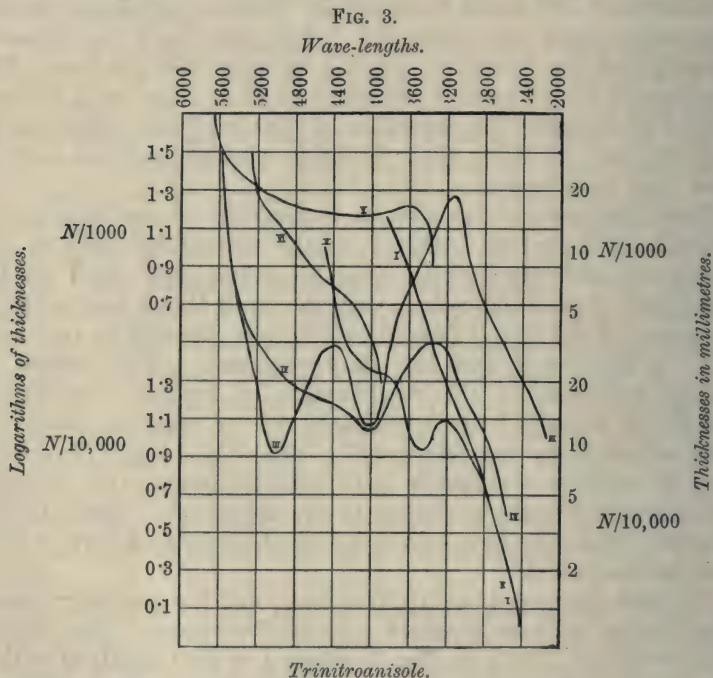
It is well known that trinitrobenzene tends to form compounds with sodium ethoxide and with anthracene and the complex aromatic hydrocarbons generally. We venture to think that our observations afford an explanation as to why these compounds are formed. When a compound possessing a closed field is mixed with another compound possessing residual affinity of an opposite type, the closed system is opened by being interpenetrated by the force lines arising from the residual affinity of the second substance. If now the difference between the properties of the two compounds be sufficiently marked, the system formed will be found to possess characteristic properties of its own as regards solubility in an indifferent solvent, etc. In the case of trinitrobenzene and anthracene, for example, the difference between their properties is sufficiently great for the system formed between the two to be relatively stable in alcoholic solution. If strong alcoholic solutions of the two be mixed, therefore, a "compound" separates out. In

the general case the stability of this compound depends on the difference in properties between the reacting substances. Such a compound has only a stable existence when this difference is well marked, but the spectroscope is able to detect the mutual influence of the two substances when the difference in their properties is far too small to produce a stable compound of the two. When the difference between the properties of the two reacting substances is increased, the resulting compound becomes more and more stable until finally we arrive at salt-formation. There is therefore no need to conceive of any break in continuity between the simple mutual influence between two substances which can only be detected optically and the formation of a salt between acid and base. The spectroscope would seem, therefore, to afford a far more delicate method of detecting the formation of loose additive compounds or their tendency to form, than the other physical methods such as those used by Kremann.

These observations also give an explanation of the nitration of aromatic hydrocarbons. Owing to the mutual influence of the nitro-group and the benzene ring, the nitric acid opens up the closed field of the hydrocarbon, with the result that a loose additive compound of the two is formed, which then proceeds to rearrange itself, giving water and the nitro-compound. The process is exactly analogous to the sulphonation of aromatic compounds, which has already been investigated by us, and in which the intermediate phase was observed (T., 1912, **101**, 1475). The formation of additive compounds with trinitrobenzene and aromatic hydrocarbons is quite analogous to the first stage in the nitration reaction, when the nitric acid and aromatic substance form a loose additive compound.

We have also examined trinitroanisole, and the results are somewhat similar to those obtained with trinitrobenzene. The absorption curves are shown in Fig. 3, where I is that obtained with a freshly-prepared solution of the recrystallised colourless compound in alcohol. This curve does not agree with that observed by Buttle and Hewitt (T., 1908, **95**, 1755), and is very similar to that of trinitrobenzene in the same solvent. The curve given by Buttle and Hewitt lies nearer to the red than ours, and the reason of this will be explained below. The addition of sodium ethoxide to the alcoholic solution at once produces a fine red colour, and the absorption spectrum is now shown by curve III in Fig. 3. Two bands are shown here, which closely approximate to the two bands obtained with trinitrobenzene under the same conditions. The solution of trinitroanisole in piperidine is also strongly coloured, and its absorption is shown by curve IV in Fig. 3. The more refrangible absorption band of the alcoholic sodium ethoxide

solution is also evidenced here, whilst the less refrangible band is reduced to a step-out. The difference in these absorption curves shows that trinitroanisole is less easily opened up than trinitrobenzene. This is more strikingly shown by the absorption exhibited by the solution in dimethylaniline and in the benzene-anthracene mixture. In the case of trinitrobenzene very well marked absorption bands are shown, but with trinitroanisole there is evidence of much less absorption (curves V and VI, Fig. 3). The dimethylaniline solution of trinitroanisole shows only a very shallow band,



- | | |
|---|--------------------------------|
| I. In alcohol (fresh). | IV. In piperidine. |
| II. In alcohol after exposure to light. | V. In dimethylaniline. |
| III. In sodium ethoxide. | VI. In benzene and anthracene. |

which, however, resembles the bands given by trinitrobenzene in that it extends over the same wave-lengths as the absorption bands of the alcoholic sodium ethoxide solution. The benzene-anthracene solution also shows evidences of absorption over the same region, but the band has given place to a very shallow step-out.

When trinitroanisole has been kept for some time, it becomes yellow, but may be obtained colourless after recrystallisation. The existence of two forms with the same melting point seems already to have been recognised (Hantzsch, *Ber.*, 1906, **39**, 1084), and it

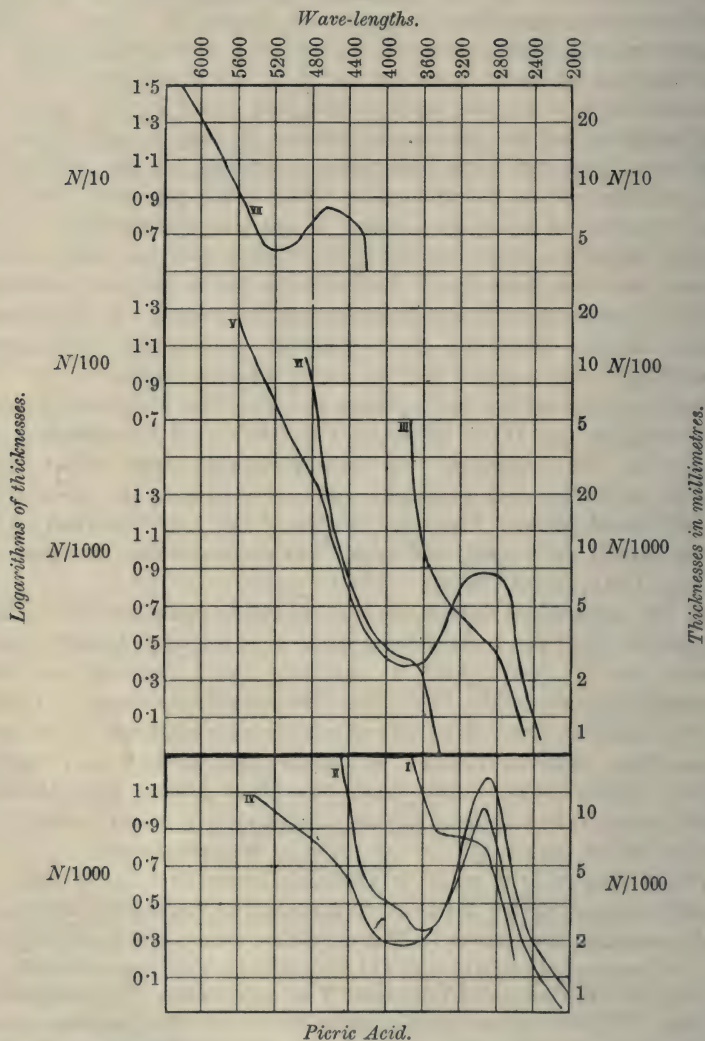
is interesting to note that the two forms have different absorption spectra. If the freshly prepared colourless solution in alcohol is kept, especially if left in the light, it turns strongly yellow, and the absorption spectrum is shown by curve II, Fig. 3. There is now one well-marked absorption band at a wave-length of $360\text{ }\mu\mu$, and there is, moreover, a step-out or incipient absorption band over the same region as the more refrangible band of the piperidine and alcoholic sodium ethoxide solutions. It may be said here that this form gives the same absorption spectrum, on the addition of sodium ethoxide, as the colourless form, which proves at once that the formation of the yellow colour is not due to hydrolysis. Altogether, therefore, there are three absorption maxima with trinitroanisole, and this substance is thus capable under suitable conditions of absorbing three different quantities of free energy. Four different phases of this compound must therefore be capable of existence according to the amount of free energy that is supplied to it. The colourless solid variety is that form in which the maximum possible condensation has taken place in the force field surrounding the molecules. By supplying free energy to this, three other forms can be produced, and represent different stages in the opening up of this closed system. The wave-lengths of the light absorbed by the three opened up phases, and which are characteristic of them, are $510\text{ }\mu\mu$, $410\text{ }\mu\mu$, and $360\text{ }\mu\mu$.

If the alcoholic solution of the colourless modification is kept exposed to light for a short time until it is coloured faintly yellow, that is to say, until only a relatively small fraction has been converted to the yellow form, then the absorption curve is shifted a little towards the red at the greater concentrations. The curve then agrees with that given by Buttle and Hewitt, and already noted. There is no doubt, therefore, that Buttle and Hewitt's observations referred to a solution containing a small quantity of the yellow or partly opened up form of trinitroanisole.

Picric acid differs from trinitroanisole in that it is still less readily opened up by alkaline solvents. The absorption curves of this compound are shown in Fig. 4, where curve I is that of picric acid in heptane, II in alcohol, III in alcoholic hydrogen chloride, IV in concentrated sodium hydroxide, V in piperidine, VI in dimethylaniline, VII in benzene containing anthracene. The two first curves are those given by the colourless and yellow modifications of picric acid, and we may point out the close resemblance between the form of the absorption curves given by the latter and that given by the yellow form of trinitroanisole (curve II, Fig. 2). The same conclusion is therefore to be drawn as to these two modifications of picric acid as in the case of trinitroanisole. The colourless variety is the completely closed form, whilst the yellow form, containing more

free energy, is the first stage in the opening up of the closed form. Hantzsch attributes the *aci*-constitution to this yellow form, but

FIG. 4.



- | | |
|----------------------------|---------------------------------|
| I. In heptane. | V. In piperidine. |
| II. In alcohol. | VI. In dimethylaniline. |
| III. In alcoholic HCl. | VII. In benzene and anthracene. |
| IV. In concentrated NaOEt. | |

we would point out that this view is untenable, inasmuch as exactly the same phenomenon holds in the case of trinitroanisole, where the *aci*-form is ruled out.

An interesting fact about picric acid is the readiness with which it gives the yellow form in alcoholic solution compared with trinitroanisole, whereas the latter gives at first a colourless solution in alcohol, which under the influence of light passes into the yellow form; the former at once gives the yellow form, or first stage in the opening up, in alcohol.

When an alcoholic solution of picric acid is treated with sodium ethoxide in equivalent quantities, no change in the absorption is noticed, as already pointed out by Buttle and Hewitt. They attribute this to the fact that the salt will be so strongly ionised that the absorption will be that of the picric ion. The ionisation will, however, be much less in alcoholic solution, and yet even here no change is observed on the addition of an equivalent of sodium ethoxide. Buttle and Hewitt say, moreover, that in all probability the picric ion will be derived from the *aci*-form, and therefore the absorption would in that case be that of the *aci*-form. When, however, a very concentrated solution of sodium hydroxide is used as solvent for the picric acid, the absorption is changed, for signs of a new absorption band begin to make their appearance over the same region as the band given by picric acid dissolved in the benzene-anthracene mixture. Now undoubtedly this absorption is due to the undissociated sodium salt, and if the absorption of the solution with one equivalent of sodium ethoxide is due to the *aci* or quinonoid ion, to what is the incipient new band due? This incipient band is given in less degree by a piperidine solution of picric acid, and very completely by the solution in the benzene-anthracene mixture. It appears that the conception of the *aci*-form is unable to explain the results. The same explanation is applicable here as in the case of trinitrobenzene and trinitroanisole. The various absorption bands are due to the existence of different stages in the opening up of the closed fields surrounding the picric acid molecule, each stage being characterised by an absorption band. As picric acid shows evidences of two absorption maxima, so two different stages in the opening up are present in equilibrium in this solution. Then again there is the more completely opened up form which is readily obtained in solution in the benzene-anthracene mixture, and much less readily in solution in concentrated sodium hydroxide or in piperidine. Altogether, therefore, we have to recognise the existence of four phases of picric acid. First, the colourless or completely closed form; secondly, the two forms which co-exist in alcoholic solution and in solution in strong sodium hydroxide; and finally the fourth form, which exists in greatest amount in solution in the benzene-anthracene mixture. The absorption maxima characteristic of the three last forms are approximately 359 μ , 408 μ , and 516 μ . The last phase

is the most completely opened up condition of picric acid yet obtained.

The following table shows the various absorption maxima possessed by trinitrobenzene, trinitroanisole, and picric acid, and as the existence of each one marks a definite stage in the opening up of the closed force field, they represent the wave-lengths of the light energy absorbed by these forms:

	4.	3.	2.	1.
Trinitrobenzene	600	515	430	— $\mu\mu$
Trinitroanisole	—	510	410	360 $\mu\mu$
Picric acid.....	—	516	408	359 $\mu\mu$

The variations in the wave-lengths of the various maxima obtained with the three compounds is not large. It will be noticed that trinitrobenzene gives one maximum (600 $\mu\mu$), which the other two do not. This absorption maximum, as previously pointed out, is obtained with dimethylaniline as solvent, and corresponds with a more complete stage in the opening up than we have yet been able to observe in the case of the other two compounds. This fact agrees with what has already been pointed out, namely, that trinitrobenzene is most easily and picric acid least easily opened up by the three substances.

Since this paper was written, a communication by Clarke, Macbeth, and Stewart has been published (P., 1913, **29**, 161), in which they deal with the colours given by tetranitromethane with substances possessing various types and degrees of residual affinity. It would seem that these are due to similar phenomena, as described above, namely, the opening up of the closed system of the complex nitro-compounds by the force lines due to the various residual affinities with which it is treated.

In considering the absorption of light by any organic compounds it must be remembered that the light is doing work on the compound. When a solvent opens up the closed system of a solute and the mixture absorbs definite wave-lengths of light, this light is doing work, and increases the effect due to the solvent. The solvent alone brings about an equilibrium between the less closed and less opened phases, and the light when it is absorbed increases the effect of the solvent, that is to say, it shifts the equilibrium towards the more opened form. In other words, a photodynamic equilibrium is set up. This point of view was brought out in our previous paper (this vol., p. 91), where we showed that when the mass of solvent is increased beyond a certain limit the amount of light absorbed tends to decrease, and in the case of ethyl acetate it is easy to reach a dilution at which the light absorption vanishes. This phenomenon will be observed when the equilibrium is carried so far in one direction by the solvent that there is no

work left for the light to do. Perhaps this may be made clearer by reference to a specific case, in which the light has actually been proved to do work. Certain cases have been observed in which the electrical conductivity, and hence the ionisation of a solution, is increased by light. The equilibrium between dissociated and undissociated molecules is shifted towards the side of dissociation by light. If such a solution were diluted until the ionisation were practically complete, then the amount of light absorbed would be very small indeed compared with that absorbed by an equimolecular layer of the stronger solution.

When the closed force field of a substance is opened up it absorbs free energy and becomes endowed with chemical reactivity. Again, when the system is entirely closed the reactivity is vanishingly small, and as the systems are opened up by the addition of definite quantities of free energy the reactivity is enhanced by definite amounts. In the cases where ionisation takes place the reactivity of the system is usually attributed to the ions, but it would seem preferable to consider that the reactivity is a property of the whole system, and that the formation of the ions is a phenomenon which is secondary in the sense that it is a function of the enhanced reactivity arising from the conditions under which the salt exists. This point of view has already been discussed for the cupric salts by Garrett (*Zeitsch. Elektrochem.*, 1913, **19**, 1).

THE UNIVERSITY, LIVERPOOL.

CCXXII.—*The Fractionation of Alloys and Minerals in the Electric Micro-furnace.*

By ARNOLD LOCKHART FLETCHER.

THE following apparatus, for which the name "Micro-furnace" * is proposed, has been employed in the distillation at high temperatures of various inorganic substances, including alloys, minerals, and ores.

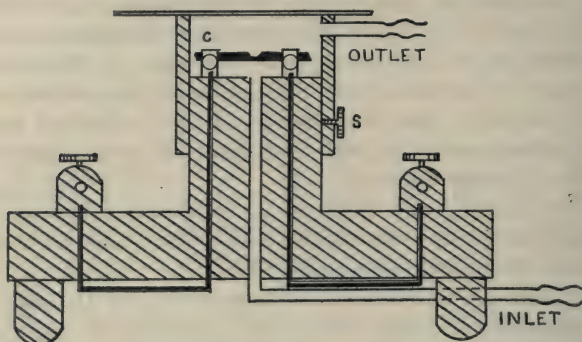
It consists of a brass drum sliding over a solid slate cylinder from 5 to 8 cm. in diameter, bearing a pair of terminals for a carbon rod,† which can be heated rapidly to extremely high temperatures by the passage of an electric current. These terminals

* For assistance in designing the most convenient form of this furnace, I am indebted to my father, Mr. G. Fletcher.

† Carbons of small sectional area suitable for the qualitative application of this instrument have been obtained from the Le Carbone Co., London.

are most conveniently made in the form of horizontal clock springs, which press the carbon down on a block of copper or graphite

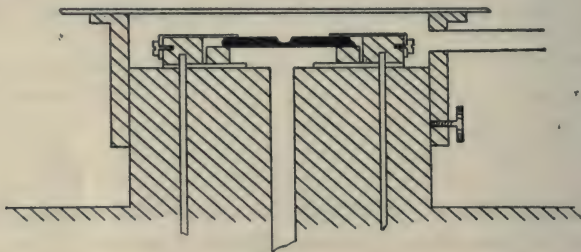
FIG. 1.



MICRO - FURNACE

resting on a copper strip connected to the terminals, as shown in Fig. 2. The carbon may be protected or partly enclosed when desirable by loose, closely placed parallel carbons. The general arrangement is shown below:

FIG. 2.



SUBLIMATION CHAMBER or MICRO - FURNACE

In the above figure the carbon rod and terminal connexions are for the sake of convenience placed diametrically, the terminals being shown turned through a right angle. In practice, however, they may be arranged with the carbon at right angles to the spring clips, forming with them three sides of a rectangle, thus reducing the size of the chamber. The sliding cylinder is covered by a receiving plate of glass, clear or opaque silica, or biscuit ware. The space surrounding the rod can be filled with various gases or rendered partially vacuous by means of inlet and outlet tubes, the former perforating the slate support, whilst the latter is fixed below the upper rim of the brass cylinder. The spring clips holding the rod are easily manipulated during the frequent

changes of the carbon by removing for a moment the sliding drum. This drum may be set in any position on the slate cylinder by means of the screw *S*, and thus the size of the chamber, and the distance between the carbon and cover plate, regulated at will. The inlet tube which opens under the heated particle tends to transport heavy vapours to the receiving plate.

Carbon appears to be the most satisfactory support for the material under examination because (*a*) it may be raised to the highest attainable temperatures, (*b*) it prevents oxidation when desirable, (*c*) it does not contain impurities likely to affect the analytical results, and does not usually combine with or adhere to the molten metal, and hence non-volatile residues may be removed for gravimetric purposes.

As examples of the application of this furnace to qualitative analysis, the following table is presented, showing the colours obtained in air on glass or transparent silica:

Family.	Element.	Deposit.	Family.	Element.	Deposit.
I.	Copper	red, green, yellow.	V.	Vanadium	yellow-green.
	Silver	dull grey, some pink.		Columbium	white.
	Gold	red, violet to purple, gold.		Tantalum	white.
II.	Glucinum	white.		Arsenic	white.
	Magnesium	white.		Antimony	white.
	Zinc	white.		Bismuth	yellow.
III.	Cadmium	red-brown.	VI.	Chromium	green.
	Mercury	grey-white.		Molybdenum	pale yellow.
	Aluminium	white.		Tungsten	white.
	Indium	pale yellow.		Uranium	black.
IV.	Thallium	red and white.		Selenium	red.
	Titanium	white.	VII.	Tellurium	white.
	Zirconium	cream.		Manganese	light brown.
	Cerium	white.	VIII.	Iron	red-brown.
	Silicon	white, some yellow.		Cobalt	black.
	Tin	white.		Nickel	black.
	Lead	yellow.		Ruthenium	grey.
				Platinum	black.

The following table represents the colour of deposits obtained (*a*) in the presence of hydrogen sulphide, (*b*) by distillation on a plate on which iodine has been previously sublimed:

Element.	Deposit in hydrogen sulphide.	Deposit on plate bearing iodine.	Element.	Deposit in hydrogen sulphide.	Deposit on plate bearing iodine.
Copper	green-black	white.	Tin	black and yellow	orange-brown.
Silver	black	pale yellow.	Lead	blue-black	deep yellow.
Gold	—	yellow-brown.	Arsenic	red, yellow	deep yellow.
Zinc	white	white.	Antimony	red	orange-red.
Cadmium	yellow	white.	Bismuth	brown, black	chocolate.
Mercury	black	scarlet and yellow.	Selenium	red	black.
Indium	red-brown	yellow.	Tellurium	black	chocolate.
Thallium	black, red and brown	orange-brown.			

In dealing with refractory substances, such as steels and iron alloys, two difficulties were encountered: the decrepitation of the fusion at high temperatures, and the rapid burning of the carbon. The first of these may be overcome by placing strips of carbon or biscuit ware against the rod, so that the fusion is unable to escape, or by using larger carbons and heavier currents, and the second to some extent by using larger carbons partly protected. The rod should not be wholly embedded, as, in the absence of free oxygen, a deposit of carbon interferes with the distillation. For high temperature work the most suitable size of the rod is from 8 to 30 sq. mm. cross-section. This is reduced at the centre according to the current available.

Quantitative Separations in Air.

The general behaviour of many metals when heated in depressions in the carbon of the micro-furnace in the manner described suggested the possibility of obtaining quantitative results by this method. From the experiments so far carried out, it appears that the micro-furnace is capable of yielding quantitative results with an accuracy which depends on the nature and relative quantities of the constituents of the alloy. It has been recently shown (Turner, *J. Inst. Metals*, 1912, **12**, Jan., and Groves and Turner, *T.*, 1912, **101**, 585) that quantitative separations may be carried out on certain alloys by heating for some time in a vacuum up to 1200° in the electric furnace. By the process to be described, the method may be extended to include in certain cases alloys which are stable at the temperature limits of the tube furnace. A small weighed filing—say, 4 or 5 milligrams—of the alloy is placed in the hollow of the carbon rod, which is then covered with a fragment of transparent silica, and the temperature of the strip is raised slowly until the deposition of one constituent is observed on the cover plate. The temperature is then steadied for a short time until this has ceased, when the circuit is broken and the rod cooled. An inspection of the colour and nature of the deposit shows whether the constituent has volatilised *per se*. To aid this inspection a number of such deposits should first be prepared. This operation is then repeated as often as necessary, and the remaining globule weighed. This method possesses certain advantages over one in which the sublimate is weighed, and which therefore involves an assumption as to the chemical nature and uniform character of the deposit. A further heating will indicate whether the fractionation has been satisfactorily accomplished. If not, further weighings must be made. The final residue should be volatilised, as this method often reveals traces of unsuspected

impurities. When a separation is incomplete, a rough approximation to the proportions present may be made by inspection, or from weighings taken at some points between the appearance of the second, and disappearance of the first, constituent.

A quantitative separation can only be carried out in cases where the substances or their compounds with the surrounding atmosphere differ greatly in volatility. In practice, the following difficulties arise: (1) One constituent is mechanically retained by another, and is thus difficult to volatilise; thus, although tin and lead are partly separable, they are difficult to separate owing to the retention of lead inside the fusion. This is to some extent overcome by repeated heating and cooling, aided by intermediate stirring of the soft fusion, whereby the lead is brought to the surface. (2) The alloy does not assume the spherical condition. This is often the case with alloys containing aluminium, which tends to powder. (3) Oxidation. When the sublimate oxidises freely it tends to transport portions of the residue. The presence of much oxide in the residue introduces an error into the calculation. In most cases this may be prevented by the use of large carbons or by partly surrounding the rod with parallel graphite or carbon rods; in others the separation should be carried out in hydrogen or coal gas.

There is in practice usually a tendency towards underestimating the residue, and this is enhanced as the volatilities of the substances under the conditions of the separation approximate; for example, copper and nickel are difficult to separate quantitatively. Analyses are in general most easily carried out in alloys in which the constituent most freely volatile is present in the smallest relative quantity. The micro-furnace will find its chief use as a powerful means for ascertaining rapidly what elements are present in any alloy, mineral or ore, and roughly in what proportions they are present.

The following is a list of alloys on which quantitative separations have been attempted:

Brass.

- | | | | | |
|----|--------|--|---------|-----------|
| 1. | 0·0031 | yielded after distillation of zinc a residue | 0·0019. | Cu 61·29. |
| 2. | 0·0049 | „ „ „ „ | 0·0030. | Cu 61·23. |

Brass (Cu, 64·32; Zn, 35·68; Ni, 2·85; Fe, 1·76).

- | | | | | |
|----|--------|--|----------|-----------|
| 1. | 0·0073 | yielded after distillation of zinc a residue | 0·0050. | Cu 68·49. |
| 2. | 0·0063 | „ „ „ „ | 0·0043. | Cu 68·25. |
| 3. | 0·0058 | „ „ „ „ | 0·00395. | Cu 68·10. |

Bismuth-Zinc (Bi, 50; Zn, 50).

1.	0.0022	yielded after distillation of zinc a residue	0.0012.	Bi	54.5.
2.	0.0036	" " " " "	0.0016.	Bi	44.5.
3.	0.0022	" " " " "	0.0010.	Bi	45.5.

Ferro-zinc (Zn, 95; Fe, 5).

1.	0.0071	yielded after distillation of zinc a residue	0.0004.	Zn	94.4.
2.	0.0150	" " " " "	0.0011.	Zn	92.7.

Ferro-manganese (Mn, 90; Fe, 10).

A rough approximation to the proportions of the constituents present in the more refractory alloys may be made by an inspection of their sublimates. The separation of iron and manganese which occurs by the removal of the manganese as the buff oxide is tedious when the manganese is present in large proportions. A manganese containing about 10 per cent. of iron was treated in the furnace. A free evolution of manganese oxide at first takes place, becoming less copious in succeeding distillations until a slight residue is left, consisting chiefly of iron. The following results were obtained:

1.	0.0025	gave after distillation of manganese a residue	0.0005.	Mn	80.0.
2.	0.0033	" " " " "	0.0004.	Mn	87.9.
3.	0.0036	" " " " "	0.0007.	Mn	80.6.
4.	0.0070	" " " " "	0.0007.	Mn	90.0.
5.	0.0081	" " " " "	0.00095.	Mn	88.3.
6.	0.0027	" " " " "	0.0002.	Mn	92.6.
7.	0.0019	" " " " "	0.0004.	Mn	78.9.

The difficulty of this separation is further increased by the similarity in the deposits of small quantities of the oxides of iron and manganese.

As illustrative of the delicacy of detection of certain elements, it may be pointed out that the zinc present in 0.0005 gram of bronze coinage is quite easily visible when distilled on to glass, the actual quantity being only 5×10^{-6} gram. Previous experiments have shown that lead and arsenic can be detected in quantities of the same order of magnitude (Fletcher, *Sci. Proc. Roy. Dubl. Soc.*, 1913, **13**, 460).

The following are particulars of experiments showing analyses of residue and sublimate:

Brass (Cu, 65.23; Zn, 33.95; Fe, 0.82; Sn, trace).

Owing to the difficulties arising in analysing by this method, quantities suitable for gravimetric estimation which would necessitate larger carbons and disproportionately heavier currents, the residues from several separate analyses were examined together.

Conditions of Experiment.—The temperature was raised until distillation appeared nearly complete, when the current was cut off for examination of the sublimate. The residue was then re-heated until the sublimate showed traces of copper. Approximate total time of heating, one to two minutes in several periods of some seconds. Approximate temperature, 900° , rising in successive sublimations to about 1500° for the last traces of zinc. Percentages of residual copper obtained: 66.44, 65.16, 66.08, 64.65, 67.60; mean, 65.99.

In the tables the first column gives the composition obtained from two previous, and sometimes independent wet analyses. The second column gives the total weight of residues analysed, with the quantities of the original constituents contained therein. The last two columns show the analyses of residue and sublimate respectively, calculated to show the percentages on the original alloy. The portion "unaccounted," obtained by difference, does not involve a large actual error, and probably represents a deficiency in the analysis, in which case the analyses of residue and sublimate may be regarded throughout as satisfactorily complementary, and in very fair accordance with the results obtained.

Wet Analyses.

Initial brass.	Residue 0.2505.	Per cent. on original weight.	Sublimate per cent. on original weight.
Cu 65.23	0.2283	60.00	1.79
Zn 33.95	trace	—	32.23 (diff.)
Fe 0.82	"	—	none
Sn trace	"	—	"
Unaccounted	0.0222	5.08	—

The result should show from this a net excess of less than 3.29 per cent. It shows, in fact, a deficiency of only 0.06 on the wet analysis.

Brass * (Cu, 64.32; Zn, 35.68; Ni, 2.85; Fe, 1.76).

Conditions of Experiment.—Six separate quantities of average weight 0.08704 were treated. They were raised to the required temperature range (about 1200°) on a carbon rod 7 mm. in diameter, filed to the core in the centre, by a current of 25 amperes. The time of heating was in all one to two minutes in periods of about twenty seconds, with intermediate cooling for examination. The percentages of residue in each case were: 65.69, 65.58, 66.60, 68.70, 68.14, 68.35; *mean, 67.18. This average compares favourably with the previous mean result on three analyses of 68.37.

* Same specimen as previously examined.

Wet Analyses.

Initial brass.	Residue 0.3512.	Per cent. on original weight.	Sublimate per cent. on original weight.
Cu 64.32	0.3073	58.84	2.42
Zn 35.68	none	—	32.54 (diff.)
Ni 2.85	0.0100	1.91	none
Fe 1.76	0.0062	1.19	0.17
Unaccounted	0.0277	5.31	—

The unaccounted portion is partly explicable on the retention of carbon in the residue (apparent on subsequent solution) and the slight partial oxidation of the surface film of the residual pellets. The combined effect of these errors is very small, amounting on several close experiments with similar quantities of copper to only 0.5 per cent., the remaining deficiency of about 4.8 per cent. being probably accounted for in the loss on analysis. An examination of these numbers shows that the analysis should yield an excess percentage of the refractory constituents of 5.31, and a counter-acting deficiency of 2.59, due to the volatilisation of the copper and iron found in the sublimate. This leaves a net result of 2.72 per cent. of excess. There is, in fact, a deficiency of 1.75 per cent. in the estimation of the residual constituents. The errors of excess and deficiency in practice nearly balance one another, and in the previous experiments already cited the error amounted only to 0.56 per cent. The figures are satisfactorily close in view of the small quantities dealt with, and seem to indicate the possibility of a brass analysis by this method to within 1 or 2 per cent.

Tin-Lead Alloy (Sn, 48.94; Pb, 51.06).

Particulars of Experiment.—This alloy can only be analysed under conditions allowing of free access of air, as the separation depends on the oxidation of the lead and the removal of its oxide. This is best done by using small quantities. Five portions, amounting in all to 0.2606 gram, were analysed. Each portion was heated in four or five separate periods of twenty to thirty seconds to a temperature of about 1000°. The evolution of litharge was at first copious, and finally scarce, and mixed with stannic oxide. The results obtained were: tin, 42.31, 40.00, 41.66, 42.86, 41.09; mean, 41.58.

Wet Analyses.

Initial alloy.	Residue 0.10835.	Per cent. on original weight.	Sublimate per cent. composition.
Sn..... 49.40	0.09963	38.23	7.11
Pb..... 50.60	trace	—	51.12
Unaccounted	0.00872	3.35	—

The conclusion from these results is that a 50 per cent. alloy

of these metals is not capable of analysis by this method in air to within 8 or 9 per cent. If we assume the unaccounted portion to be mainly due to deficiency of analysis, then in an alloy of these proportions about 7 per cent. of tin passes into the sublimate. The actual deficiency on five experiments was 7.82. The error will be increased or diminished directly according to the proportion of lead.

Tin-Lead Alloy (Sn, 82.12; Pb, 17.88).

Conditions of experiment the same as before. Nine separate fractionations were made, using small quantities, and similar difficulties were experienced. The results obtained were: tin, 76.32, 77.50, 73.53, 75.91, 78.18, 73.47, 79.26, 75.36, 78.69; mean, 76.47. A wet analysis yielded the following results:

Wet Analyses.

Initial alloy.		Residue per cent. on original.	Sublimate per cent. on original.
Sn	82.12	76.24	4.3
Pb	17.88	0.3	18.3

It appears from these numbers that with lead-tin alloys in which the lead is below 20 per cent. the separation can be effected by distillation in air to within about 6 per cent. The actual deficiency on nine fractionations was 5.65, and the analysis showed 4.3 per cent. of tin in the sublimate.

Aluminium-Cadmium (Al, 86.67; Cd, 13.33).

Conditions of Experiment.—The filing is heated slowly to about 1000° for some fifteen to thirty seconds, when the cadmium distils off freely. Although the separation is in most cases fairly complete, the tendency of this alloy to decrepitate during the evolution of cadmium prevents an accurately quantitative analysis. About 2 centigrams were used for each fractionation, and the following results were obtained: aluminium, 79.5, 85.7, 88.5, 86.3, 78.3, 86.5, 82.4, 84.6, 86.4; mean, 84.24. A number of deficient results are excluded.

Wet Analyses.

Initial alloy.		Per cent. on Residue 0.1379. original weight.		Sublimate per cent. on original weight.
Al	86.67	0.1302	80.0	0.2
Cd	13.33	0.0077	4.5	16.0

The wet analyses were made on all the residues, among which were particles, which owing to decrepitation had been insufficiently heated, and yielded abnormal results. The amount of cadmium retained is therefore usually below the 4.5 per cent. above.

Mineral Analysis.

Perhaps the most useful possibility for the micro-furnace lies in its application to the rapid determination of minerals of doubtful identity, in which field of work its value is enhanced on account of the small quantities necessary for an analysis, and the ease and simplicity with which such analysis is carried out. An inspection of the foregoing deposits resulting from the distillation of the constituents of a mineral from carbon at high temperatures is frequently sufficient for its determination without a gravimetric separation, and with some practice such analyses can be made with a fair amount of accuracy owing to the concentric arrangement of the deposits according to their relative volatilities. The following results are given in illustration of its application in this respect. The analyses occupied in each case a few minutes only.

Sylvanite.

1. 0.00365 yielded after distillation 0.0016.	Te 56.1.
A second distillation yielded chiefly silver 0.00095.	Ag 17.8.
The residue separated mechanically into gold	Au 21.9.
and some impurity resembling silica.	Impurity 4.2.

There is a tendency to a mechanical separation of silver from the gold in the residue from the distillation of the tellurium:

2. 0.00765 yielded after distillation 0.00365.	Te 52.3.
	Au and Ag 47.7.

Psilomelane.

0.0024 gave after distillation a residue of	Mn 0.0018.	Mn 75.
0.0041 " " " "	Mn 0.0029.	Mn 71.
0.0010 " " " "	Mn 0.00075.	Mn 75.
0.0045 " " " "	Mn 0.00325.	Mn 72.
0.0031 " " " "	Mn 0.0023.	Mn 74.
0.0087 " " " "	Mn 0.0065.	Mn 75.

The above rough approximations to the percentages of the minerals dealt with, together with the characteristic appearances of the deposits produced by each mineral, would be of very great assistance in identifying the mineral.

Sufficient has been said to indicate both the value and the limitations of the method. The possibility of a separation is in most cases bound up with the relative volatility of the metal or its compound formed under the influence of the particular atmosphere in which the distillation is made. As yet only a few alloys have been examined, and those in air, and it is hoped that the method may find extension both in its application to the qualitative analysis and determination of minerals by their characteristic sublimates,

and in the more accurate quantitative separation of metals under the influence of atmospheres other than air.

I am indebted to Professor G. T. Morgan and to Dr. J. H. Pollok for their continued interest in the course of these experiments, and to Professor Grenville A. J. Cole for the mineral specimens examined.

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CCXXIII.—*Resolution of α -Anilinostearic Acid.*

By HENRY RONDEL LE SUEUR.

THE resolution of α -anilinostearic acid was undertaken in order to obtain an optically active amphoteric substance, which was required for an investigation with which the author has been engaged for some time. It was essential that the active substance should be not only feebly amphoteric, but also insoluble in water and in organic solvents generally, and both of these conditions are fulfilled by α -anilinostearic acid.

At the outset the fractional crystallisation of the quinine salt of the anilinostearic acid was carried out, but although the salt was recrystallised ten times, the free acid obtained from it had very little optical activity. It was then found that dissociation of the quinine salt took place during the recrystallisation, with the result that the solid which separated out from the solution on cooling consisted largely of the free acid. Thus, in one experiment, 7.5 grams of what was supposed to be the true quinine salt gave 6.5 grams of free acid after removal of the quinine, and this is far in excess of what should have been obtained even if the quinine had acted as a diacid base. To overcome this difficulty, due to dissociation, the alkaloidal salt was recrystallised from solutions containing a large excess of the free alkaloid, but although a better result was obtained, nevertheless a complete resolution was not effected by this method. Thus, in one experiment, 45 grams of anilinostearic acid and 90 grams of quinine were dissolved in one litre of hot alcohol, and the solution kept at 5° for several days, at the end of which time 78 grams of the quinine salt were obtained. These were recrystallised from alcohol containing an amount of quinine equal to half the weight of the

quinine salt, and after repeating this process seven times, a dextro-acid was obtained, having an optical activity of $[\alpha]_D + 11.5^\circ$ in pyridine. This result was not regarded as satisfactory, and attempts were made to effect the resolution by means of morphine and cinchonine, but with no better results, and the idea of using alkaloids had to be abandoned.

Experiments were then made with *l*-menthylamine as a base, and it was found that this substance forms a well-crystallised and stable salt with α -anilinostearic acid, and by means of this base the desired resolution was effected. For this purpose 35 grams of α -anilinostearic acid and 14 grams of *l*-menthylamine were dissolved in a mixture of 250 c.c. of alcohol and 30 c.c. of ethyl acetate, and the solution kept in a cold place. The menthylamine salt gradually separated out in aggregates of long, flat needles, and at the end of eight days these were collected (filtrate *A*), and after drying weighed 17 grams. These were then recrystallised once from a mixture of alcohol and ethyl acetate, and then from alcohol alone until the activity of the acid, which was dextrorotatory, was not increased by further recrystallisation. That the resolution was complete was further proved by recrystallising the acid itself, when it was found that both its melting point and rotatory power were constant.

Pyridine was used for determining the rotation of the acid, as it is quite insoluble in water, and its solubility in the ordinary organic solvents in the cold is far too small to admit of their being used for this purpose. The values thus obtained are consequently those of the pyridine salt in solution in pyridine:

0.4648 of acid, dissolved in pyridine, made up to 15 c.c., and examined at 19° in a 2-dcm. tube, gave $\alpha_D^{19} + 2.15^\circ$, whence $[\alpha]_D^{19} + 34.7^\circ$.

The *d*-anilinostearic acid is sufficiently soluble in alcohol at 40° for its rotation to be determined in this liquid at this temperature, and for the determination under these conditions the author is indebted to Mr. G. W. Clough, who obtained the following result:

$l = 4$; $c = 0.6037$; $\alpha_D^{40} + 0.45^\circ$, whence $[\alpha]_D^{40} + 18.6^\circ$ in solution in alcohol.

d- α -Anilinostearic acid, $C_{16}H_{33} \cdot CH(NHPh) \cdot CO_2H$, is insoluble in light petroleum, chloroform, or benzene in the cold, sparingly so in cold ether, ethyl acetate, or acetone, and moderately soluble in hot alcohol, from which it crystallises on cooling in aggregates of flat needles, melting at 129 — 130° (Found, $N = 3.85$. $C_{24}H_{41}O_2N$ requires $N = 3.73$ per cent.). The melting point of inactive anilinostearic acid is 141 — 142° (T., 1910, 97, 2435).

The *l*-menthylamine salt of *d*-anilinostearic acid is readily soluble

in ether, chloroform, or benzene, and crystallises from alcohol in aggregates of long needles, flat needles, melting at 61—63°:

0.2308 gave 10.4 c.c. N_2 (moist) at 17° and 765 mm. $N=5.26$.

$C_{24}H_{41}O_2N, C_{10}H_{21}N$ requires $N=5.28$ per cent.

The filtrate *A* (p. 2109), obtained in the first crystallisation of the menthylamine salt of the inactive anilinostearic acid, was concentrated to 120 c.c., and allowed to remain for some time, when 2.8 grams of solid separated. This was collected, and the filtrate concentrated to 50 c.c., but as no solid separated the solution was poured into dilute sulphuric acid, and the precipitated acid collected, well washed and dried. After two recrystallisations from alcohol its rotation in pyridine was $[\alpha]_D^{20} -18^\circ$. The acid was recrystallised three times more from alcohol, then again converted into its menthylamine salt, and this recrystallised from alcohol. Finally, the acid was again liberated from its salt, and after three recrystallisations from alcohol melted at 128—129°, and a determination of its rotation in pyridine gave the following result:

$l=2$, $c=2.38$; $\alpha_D^{19} -1.44^\circ$; whence $[\alpha]_D^{19} -30.2^\circ$ in solution in pyridine.

l-*α*-Anilinostearic acid crystallises from alcohol in aggregates of flat needles, and its solubility in various solvents corresponds with that of its *d*-isomeride.

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CCXXIV.—*Bismuthinitrites.*

By WALTER CRAVEN BALL and HAROLD HELLING ABRAM.

IN previous communications (T., 1905, **87**, 761; 1909, **95**, 2126; 1910, **97**, 1408) one of the authors of the present paper has described several compounds of bismuth nitrite with the alkaline nitrites. These compounds were chiefly remarkable as affording a method for the gravimetric estimation of sodium, and for its separation from potassium, owing to the insolubility of caesium sodium bismuthinitrite and the non-formation of the corresponding potassium salt (T., 1910, **97**, 1408). As it is unusual to find such sharp differences in the behaviour of sodium and potassium salts, the present authors have investigated all the salts of this series which they have been able to obtain, in order to discover, if possible, other facts bearing on this difference in behaviour. The salts which have been obtained all fall into two groups, of which

the general formulæ are respectively $X_3Bi(NO_2)_6$ and $X_2YBi(NO_2)_6$. In these formulæ X represents any of the metals ammonium, potassium, rubidium, cæsium, and thallium, whilst Y stands for either lithium, sodium, or silver.

There are thus possible five compounds of the $X_3Bi(NO_2)_6$ series, or simple bismuthinitrites, and of these, four have been obtained, the attempts to obtain the ammonium salt having been so far unsuccessful owing to the great instability of concentrated solutions of ammonium nitrite in the presence of acid.

Although the ammonium salt has not been obtained, bismuthinitrites of several organic nitrogenous bases, such as cocaine and brucine, can easily be prepared.

Of the mixed bismuthinitrites of the general type $X_2YBi(NO_2)_6$, fifteen are possible; for each of the metals X might exist together in a compound with any of the three metals represented by Y. These compounds have all been obtained.

Although many attempts have been made to prepare compounds, in the solid state, containing two metals of the X series together, or two metals of the Y series together, they have been entirely unsuccessful. The same remark applies to all the attempts the authors have made to obtain compounds in the solid condition, containing two atoms of a Y series metal with one atom of an element represented by X, or to prepare compounds having the formula $Y_3Bi(NO_2)_6$. The simple bismuthinitrites of sodium and of lithium probably exist in solution, for deep orange-coloured liquids result when bismuth nitrate is added to solutions of the nitrites of these metals, just as happens in the case of potassium nitrite or of rubidium nitrite. Whereas, however, the bismuthinitrites of the two latter metals can be precipitated from their solutions, this cannot be done with lithium or sodium.

The apparent impossibility of preparing mixed bismuthinitrites containing only metals of the X series, or of the Y series, is well shown by adding cæsium nitrate to separate solutions of the nitrites of sodium and of potassium each containing bismuth. With the sodium solution there occurs an immediate precipitate of the mixed salt, sodium cæsium bismuthinitrite, even when traces only of cæsium salt are added. With the potassium solution there is no apparent change until a large quantity of cæsium has been added, when a precipitate of the simple cæsium bismuthinitrite gradually settles. Again, silver nitrate, the nitrate of an element of the Y series, when added to a solution of sodium nitrite containing bismuth, produces no deposition of a mixed compound containing two elements of the Y series, but on the addition of a potassium solution, or of a solution of any of the metals of the X series, there is at once a precipitation of the mixed X-Ag salt.

This difference in behaviour between sodium and potassium, which, as above-mentioned, is sufficiently pronounced to form a method of separating them, is now to some extent explained; for potassium, being a metal of the X series, will not form a mixed bismuthinitrite with caesium, also a metal of this series, whereas sodium, belonging to the Y series, will do so. As the caesium sodium salt is a very insoluble one, the metal can in this way be separated from potassium, collected, and weighed.*

In a similar manner, caesium and rubidium may be separated from potassium,† for on adding a mixture of salts of the three metals to a concentrated solution of sodium nitrite containing bismuth, the mixed bismuthinitrites of sodium with caesium, and of sodium with rubidium, will precipitate, being only very sparingly soluble, whilst the very soluble potassium sodium salt remains in solution. It seems, then, necessary, in order that a mixed bismuthinitrite should be capable of existence, that it should contain a metal of the isomorphous series, (NH_4) , K, Rb, Cs, Tl, together with one belonging to the isomorphous series, Li, Na, Ag, the metal of the former series being present in the greater atomic proportion.

A further series of five compounds exists, containing nickel in addition to a metal of the X series. These compounds are precipitated when a nickel salt is added to the solution of a nitrite of

* Incidentally, this explains another fact noticed in studying the estimation of sodium as sodium caesium bismuthinitrite. The reagent used contained 30 grams of potassium nitrite, 3 grams of bismuth nitrate, and about 1.5 grams of caesium nitrate per 100 c.c., and produced a yellow precipitate of sodium caesium bismuthinitrite on the addition of traces of a sodium salt. When a reagent containing less potassium nitrite was made up, it was noticed that part of the caesium would gradually deposit as caesium bismuthinitrite, more being thus precipitated the lower the concentration of the potassium nitrite. Conversely, when the reagent contained more than 30 grams of potassium nitrite per 100 c.c., it could hold more caesium salt without deposition of caesium bismuthinitrite. There would appear to be an equilibrium between the amounts formed of the very soluble potassium bismuthinitrite and of the relatively insoluble caesium bismuthinitrite, the concentration of the latter, when high concentrations of potassium nitrite were used, failing to reach the value necessary for precipitation. These facts seem to render unlikely the existence, even in solution, of a potassium caesium bismuthinitrite.

† Caesium may also be separated from rubidium by taking advantage of the greater insolubility of the caesium sodium bismuthinitrite. Thus, if a mixture of caesium and rubidium nitrates is added to a concentrated solution of potassium nitrite containing bismuth, and then a sodium salt gradually, the caesium sodium bismuthinitrite will precipitate with a very small concentration of sodium, whilst the rubidium will remain in solution until a much greater concentration of sodium is attained. One of the authors has used this method satisfactorily for separating caesium from an impure rubidium chloride obtained in the extraction of lithium. The separation has not been investigated quantitatively, and some rubidium remains in solution.

any of these metals, in presence of bismuth. The Y metals do not appear to form any mixed compounds with nickel.

The bismuthinitrites resemble the cobaltinitrites closely in formulæ, colour, and solubility in many cases; thus silver produces no precipitate with lithium or sodium cobaltinitrite, nor with sodium or lithium solutions containing bismuth (sodium and lithium bismuthinitrites), but on the addition of a salt of a metal of the X series the corresponding X-Ag cobaltinitrite or bismuthinitrite is precipitated as a yellow or red, crystalline powder.

In preparing the bismuthinitrites, chlorides should be absent, or present in only very small amount; otherwise bismuth oxychloride will precipitate.

As the bismuthinitrites are all hydrolysed by water, in most cases rapidly, it is impossible, as a rule, to wash them. They are generally prepared by precipitation from a strong solution of a nitrite, and it is, in consequence, difficult to remove all traces of mother-liquor from the preparations. The most that can be done is to remove the mother liquor as completely as possible by the aid of the pump, and then to press the crystals on porous plates. The nearly dry crystals are then kept for some hours, under pressure, between sheets of filter paper. Fortunately, the salts are highly crystalline, which renders it easier to remove mother liquor, but the difficulty of completely effecting this removal frequently shows itself slightly in the analyses; thus the thallous sodium salt, which is precipitated on adding a thallous salt to a strong solution of sodium nitrite containing bismuth, shows a rather too high percentage of sodium. This effect on the analytical results is hardly evident in the case of the less soluble bismuthinitrites, such as the silver salts, for these can be precipitated from a less concentrated mother liquor, but is chiefly seen in those which are the most soluble.

The proportions of the different salts used in the preparation of the various bismuthinitrites may, as a rule, be considerably varied, and those given are simply the amounts which the authors have found to yield good results. In a few cases, such as that of the potassium sodium bismuthinitrite, the salt is formed with difficulty, and the proportions given cannot be much departed from. Frequently the method of preparation may be reversed; thus potassium lithium bismuthinitrite may be made either by adding lithium nitrate to a solution of potassium nitrite containing bismuth, or by adding potassium nitrate to the corresponding lithium nitrite solution.

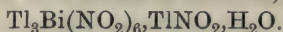
The nitrites used should be as pure and as free from alkali as possible. For convenience, the description of the various bismuthinitrites is divided into three parts. Part I describes the simple

bismuthinitrites; Part II the mixed salts; and Part III the salts containing nickel.

PART I.

The Simple Bismuthinitrites.

These salts form yellow or orange, hexagonal plates. They are less stable and more soluble, on the whole, than the mixed salts, from which they differ also in crystalline form. The potassium and rubidium salts are very unstable, as indeed are all the bismuthinitrites that contain water. In the case of cæsium, which is the most electropositive of the metals, the formula of the salt is $\text{Cs}_3\text{Bi}(\text{NO}_2)_6 \cdot \text{Bi}(\text{NO}_2)_3$, and in the case of thallium, which is the least electropositive of the metals concerned, it is



It is a curious fact that the more strongly electropositive cæsium should be able to combine with more bismuth nitrite, whereas the much less electropositive thallium should need an extra molecule of thallium nitrite in order to form its salt.

The potassium and rubidium salts have the normal formulæ $\text{K}_3\text{Bi}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$ and $\text{Rb}_3\text{Bi}(\text{NO}_2)_6 \cdot 2\text{H}_2\text{O}$, but it is possible that other hydrates of the two salts exist.

Potassium Bismuthinitrite, $\text{K}_3\text{Bi}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$.

The properties and composition of this salt were given in a former paper. It was previously prepared by passing nitrous fumes into a suspension of bismuth hydroxide in concentrated aqueous potassium nitrite, but can also be obtained by adding bismuth nitrate to a very concentrated aqueous solution of this salt.

The solution of bismuth nitrate used throughout the work described in this paper was made by warming 50 grams of crystalline bismuth nitrate with 10 c.c. of fuming nitric acid and a little water. After dissolution of the salt, the liquid was made up to 100 c.c. with water.

When some of this bismuth solution is added to four times its volume of an 80 per cent. solution of potassium nitrite, potassium bismuthinitrite is precipitated in fine, golden plates. Access of air must be avoided as much as possible, and the solution must not be cooled, for although this gives a larger yield of the salt, it leads to contamination with potassium nitrate. The salt should be collected by the aid of the pump, pressed on a porous plate, and dried finally by pressure between sheets of filter-paper.

It crystallises in large, golden-yellow or orange plates, is unstable,

and cannot be kept, at the ordinary temperature, for more than a few days. Its properties and full analyses were given in the earlier paper.

Rubidium Bismuthinitrite, $\text{Rb}_3\text{Bi}(\text{NO}_2)_6 \cdot 2\text{H}_2\text{O}$.

This salt can best be prepared by adding bismuth nitrate solution to a concentrated solution of rubidium nitrite (see p. 2131). On adding 3 or 4 c.c. of the bismuth solution to 20 or 30 c.c. of 50 per cent. rubidium nitrite solution, the salt is rapidly precipitated. It is collected and dried as for the potassium salt. It is very unstable, even more so than the potassium salt, probably because it contains two molecules of water. Other hydrates possibly exist.

It forms orange-yellow plates, which on keeping become white, with evolution of oxides of nitrogen. It is considerably less soluble than the potassium salt.

Found: $\text{Rb} = 33.56$; $\text{Bi} = 26.74$; $\text{NO}_2 = 35.44, 35.75$; H_2O (by difference) $= 4.26$.

$\text{Rb}_3\text{Bi}(\text{NO}_2)_6 \cdot 2\text{H}_2\text{O}$ requires $\text{Rb} = 33.01$; $\text{Bi} = 26.79$; $\text{NO}_2 = 35.55$; $\text{H}_2\text{O} = 4.65$ per cent.

Cæsium Bismuthinitrite, $\text{Cs}_3\text{Bi}(\text{NO}_2)_6 \cdot \text{Bi}(\text{NO}_2)_3$.

This substance can be obtained by adding bismuth nitrate solution to cæsium nitrite solution (prepared from cæsium sulphate and barium nitrite, p. 2130). It is much less soluble than the two preceding salts, so that less concentrated solutions may be used in its preparation.

It is obtained by adding one or two drops of nitric acid, then gradually 2 or 3 c.c. of bismuth nitrate solution to 20 c.c. of a 25 per cent. solution of cæsium nitrite, shaking continually. A voluminous, yellow, crystalline precipitate is formed at once, which is collected after a few minutes, and dried as for the previous salts. It may also be prepared by adding cæsium nitrate to a solution of potassium nitrite containing bismuth. To prepare it in this manner, 20 grams of the nitrite (as free from sodium as possible) are dissolved in about 40 c.c. of water; then about 7 c.c. of the bismuth nitrate solution are added, together with enough nitric acid to dissolve any precipitate (due to free alkali in the potassium nitrite) which may be produced. To the clear liquid 5 c.c. of a 10 per cent. solution of cæsium nitrate are added, and it is kept in a closed vessel (provided with a Bunsen valve for the escape of oxides of nitrogen) for several hours. Should any yellow precipitate be produced (cæsium sodium bismuthinitrite, due to traces of sodium in the reagents used) it is collected, and about 20 c.c. more of the

cæsium solution are added. The precipitate of cæsium bismuthinitrite should be collected after several hours' keeping.

It consists of golden to orange, hexagonal plates, closely resembling lead iodide. Contrary to expectation, the salt was found to give results on analysis agreeing with the formula $\text{Cs}_3\text{Bi}(\text{NO}_2)_6, \text{Bi}(\text{NO}_2)_3$, the percentages of cæsium and of bismuth being about the same, and corresponding therefore with the atomic ratio $3\text{Cs} : 2\text{Bi}$.

Found: $\text{Cs} = 33.43, 32.8$; $\text{Bi} = 33.80, 33.4$; $\text{NO}_2 = 33.0$.

$\text{Cs}_3\text{Bi}(\text{NO}_2)_6, \text{Bi}(\text{NO}_2)_3$ requires $\text{Cs} = 32.44$; $\text{Bi} = 33.87$;
 $\text{NO}_2 = 33.7$ per cent.

On account of the flaky nature of the crystals it is difficult to free this salt entirely from its mother liquor.

Thallium Bismuthinitrite, $\text{Tl}_3\text{Bi}(\text{NO}_2)_6, \text{TlNO}_2, \text{H}_2\text{O}$.

For this preparation it is necessary to use a solution of thallous nitrite (the preparation of this salt is described in the following paper, p. 2131) containing 20 per cent. or more of the salt. To 50 c.c. of this orange-coloured solution (the solid thallous nitrite is red) are added a few drops of acetic acid,* and then gradually 2 to 3 c.c. of the bismuth solution. A golden-yellow, crystalline precipitate is formed, which must be collected and dried as quickly as possible. Should the substance tend to decompose and turn white during its preparation, this is due to deficiency of nitrite in the solution (TlNO_2 contains less than one-fifth of its weight of NO_2), and may be remedied by the addition of a little 50 per cent. potassium nitrite solution; too much of this salt will cause the precipitate to redissolve.

The salt forms fine, golden-yellow, hexagonal plates, which have a high specific gravity. It is unstable, gradually becoming white.

Found: $\text{Tl} = 59.8$; $\text{Bi} = 15.2$.

$\text{Tl}_3\text{Bi}(\text{NO}_2)_6, \text{TlNO}_2, \text{H}_2\text{O}$ requires $\text{Tl} = 59.8$; $\text{Bi} = 15.25$ per cent.

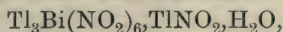
The numbers found for the bismuth and thallium agree very accurately therefore with the proportions required by the formula suggested. The same would, however, apply to the formula $\text{Tl}_3\text{Bi}(\text{NO}_2)_6, \text{TlNO}_3$ almost equally well; for in it the ratio of bismuth to thallium is the same, and the molecular weights are nearly the same. It is clear that a direct determination of the amount of nitrite present would settle which of the formulæ is correct, but, unfortunately, we were unable to devise a method for the estimation of nitrite in the presence of thallium, which should at the same time distinguish between nitrous and nitric nitrogen.

* Acetic acid rather than nitric; for thallium acetate is much more soluble than the nitrate, and therefore less likely to contaminate the precipitated compound.

The method employed throughout this work for the estimation of nitrogen was to oxidise the nitrite to nitrate by means of an excess of acid permanganate at 0° , titrating the excess of permanganate with a ferrous salt. When a thallium salt was present, this was also oxidised to the thallic state, but always incompletely. Experiments made with thalious sulphate showed that at 0° , and under the conditions used, very nearly two-thirds of the thallium was oxidised to the thallic state (or, alternatively, that the whole of the thallium was oxidised to an intermediate stage of oxidation; we have not yet had an opportunity to test the point further). If, however, both thallium and a nitrite were present, the oxidation of the thallium was more complete than if thallium alone had been present.

Thus, although it is impossible, in this way, to estimate exactly the amount of nitrite in those bismuthinitrites which contain thallium, yet by finding the amount of oxygen absorbed from permanganate it is possible to estimate the nitrite approximately.

In the case of thallium bismuthinitrite, for example, if the formula were $\text{Tl}_3\text{Bi}(\text{NO}_2)_6, \text{TlNO}_3$, the percentage amount of oxygen absorbed would be 11.75, on the assumption, never quite realised, that the thallium is completely oxidised to the thallic state. The percentage found, 12.3, was greater than this, so that this formula must obviously be incorrect. The alternative formula,



would, on the assumption of complete oxidation of the thallium, require 12.90 per cent. of absorbed oxygen. The amount of oxygen absorbed, representing that required for the complete oxidation of the nitrite plus that required for the partial oxidation of the thallium, therefore confirms the formula $\text{Tl}_3\text{Bi}(\text{NO}_2)_6, \text{TlNO}_2, \text{H}_2\text{O}$.

In the case also of the other bismuthinitrites containing thallium, the amount of oxygen absorbed is given, instead of the amount of nitrite.

PART II.

Mixed Bismuthinitrites.

These salts are, in general, less soluble and more stable than the simple bismuthinitrites. In consequence of their less solubility, they are more easily prepared. In crystalline form they differ from the plate-shaped crystals of the simple salts, forming crystals which appear to be octahedral. They vary in colour from the pale yellow of the caesium silver salt to the red of the thallium silver compound.

With the exception of those containing water of crystallisation, such as the lithium ammonium salt, they are relatively stable, and

can be kept unaltered for months. Some of them, such as the cesium sodium salt, remain unaltered at 100°. They are, however, very liable to rapid decomposition under certain conditions; for example, a large number of specimens of the various compounds which had been kept unaltered for weeks, in a store desiccator, were found to have all suffered decomposition, more or less complete, shortly after the introduction into the store vessel of a specimen of the potassium nickel salt. The decomposition appeared to be due to the slow liberation of oxides of nitrogen from the very unstable potassium nickel salt. There have been, however, other cases of the sudden decomposition of specimens that had remained for a long time unaltered, for which there were no obvious causes. On account of this instability, specimens of some of the salts were kept for some days in contact with a closed tube containing 5 milligrams of radium bromide, but there was no evidence of decomposition, nor was any phosphorescence produced. Short exposures to Röntgen radiation also produced no perceptible effect. Light acted very slowly on the silver salts, producing a gradual blackening.

For convenience, the mixed bismuthinitrites are divided into three groups: Group A containing those salts in which the metal represented by Y in the general formula $X_2YBi(NO_2)_6$ is lithium; group B, those in which Y is silver; group C, those in which Y is sodium.

Group A. Bismuthinitrites containing Lithium.

Ammonium Lithium Bismuthinitrite, $(NH_4)_2LiBi(NO_2)_6 \cdot H_2O$.

To about 16 c.c. of a 50 per cent. solution of lithium nitrite (the preparation of this salt is described in the following paper, p. 2133) are added 4 c.c. of the bismuth nitrate solution. The mixture is cooled to 0°, and about 3 grams of ammonium nitrate in 10 c.c. of water are added. After a few minutes, during which time the containing vessel is surrounded with ice, the yellow, crystalline precipitate is collected, dried on a porous plate, and then by pressure between sheets of filter-paper, as previously described.

The salt consists of fine, bright yellow crystals, probably octahedra. It is unstable, and cannot be kept at the ordinary temperature for more than a few days. Water hydrolyses it readily.

Found: $NH_4=6.70$; $Li=1.23$; $Bi=38.4$; $NO_2=50.1$; H_2O (by difference)= 3.57 .

$(NH_4)_2LiBi(NO_2)_6 \cdot H_2O$ requires $NH_4=6.62$; $Li=1.27$; $Bi=38.2$; $NO_2=50.6$; $H_2O=3.31$ per cent.

Potassium Lithium Bismuthinitrite, $K_2LiBi(NO_2)_6$.

To about 50 c.c. of a 50 per cent. solution of potassium nitrite are added between 5 and 10 c.c. of the bismuth nitrate solution, and 3 or 4 grams of a soluble lithium salt, such as the nitrate or acetate, dissolved in about 20 c.c. of water (as previously mentioned, the chloride must not be used, as it would cause bismuth oxychloride to precipitate). A yellow precipitate of the salt rapidly settles, partly on the walls of the containing vessel, and after an hour or more this is collected and dried, as in the case of the salts previously described.

The preparation may be reversed by adding the solution of a potassium salt to a solution of lithium nitrite containing bismuth.

The salt forms bright yellow, apparently octahedral crystals, resembling the ammonium lithium compound, but quite stable. It is easily hydrolysed by water. Its specific gravity at 15° is 3.21.

Found: $K=13.97$; $NO_2=48.3$.

$K_2LiBi(NO_2)_6$ requires $K=13.74$; $NO_2=48.5$ per cent.

Rubidium Lithium Bismuthinitrite, $Rb_2LiBi(NO_2)_6$.

To 20 c.c. of 50 per cent. lithium nitrite solution are added about 10 c.c. of the bismuth nitrate solution, then 2 to 3 grams of rubidium nitrate dissolved in enough water to bring the total volume to about 60 c.c.

The compound is precipitated rapidly, and may be collected after about an hour, and dried as previously described. The preparation may be reversed by adding a soluble lithium salt to a solution of rubidium nitrite to which bismuth nitrate has been added.

The salt forms yellow, apparently octahedral crystals, very similar to the potassium lithium salt in all respects, but less soluble. It is a quite stable compound.

Found: $Rb=26.8$; $Li=0.97$; $NO_2=41.34$.

$Rb_2LiBi(NO_2)_6$ requires $Rb=25.8$; $Li=1.05$; $NO_2=41.71$ per cent.

Caesium Lithium Bismuthinitrite, $Cs_2LiBi(NO_2)_6$.

To 20 c.c. of 50 per cent. lithium nitrite solution are added 5 to 10 c.c. of bismuth nitrate solution, then 2 to 3 grams of caesium nitrate in enough water to bring the total volume to about 60 c.c. The yellow precipitate is collected after about an hour, and dried as previously described.

The salt forms yellow crystals resembling those of the rubidium salt, but still less soluble. It is quite stable.

Found: $Cs=35.0$; $Li=1.00$; $NO_2=36.6$.

$Cs_2LiBi(NO_2)_6$ requires $Cs=35.1$; $Li=0.92$; $NO_2=36.5$ per cent.

Thallium Lithium Bismuthinitrite, $\text{Tl}_2\text{LiBi}(\text{NO}_2)_6$.

To 40 c.c. of a 25 per cent. solution of lithium nitrite in water about 4 c.c. of the bismuth nitrate solution are added, followed by 20 c.c. of a 10 per cent. solution of thallium nitrate or acetate, the addition being made gradually. The salt is collected after about an hour, and dried as previously described.

The colour of this salt differs considerably from those of the other bismuthinitrites, as it is pale brown. It forms bright crystals, probably octahedral. It is quite stable, and rather insoluble.

Found: $\text{Tl}=45.4$; $\text{Li}=0.84$; $\text{Bi}=23.04$.

$\text{Tl}_2\text{LiBi}(\text{NO}_2)_6$ requires $\text{Tl}=45.4$; $\text{Li}=0.77$; $\text{Bi}=23.1$ per cent.

The percentage amount of oxygen absorbed by the salt from permanganate solution at 0° was 13.8 (see p. 2117); assuming that all the thallium was oxidised to the thallic state, it should be 14.2.

Group B. Bismuthinitrites containing Silver.

These salts crystallise well, and, with the exception of the potassium-silver compound, are stable. In the series ammonium-silver, potassium-silver, rubidium-silver, and caesium-silver the solubility and the depth of colour decrease with increasing molecular weight: the ammonium silver salt is red, and the most soluble of the group, the potassium salt, is red inclining to orange, and less soluble, the rubidium-silver compound is orange and still less soluble, and the caesium-silver salt is yellow and very insoluble. The thallium-silver salt is also of very low solubility, but is red. The specific gravities of these compounds also increase with increasing molecular weight, and have the following values at $15-16^\circ$:

Ammonium-silver salt.	Found,	3.05, 3.06.	Mean, 3.055.
Potassium-silver	„	3.32, 3.34, 3.33.	Mean, 3.33.
Rubidium-silver	„	3.66, 3.68, 3.67.	Mean, 3.67.
Caesium-silver	„	3.883, 3.875.	Mean, 3.88.
Thallium-silver	„	4.860, 4.874.	Mean, 4.87.

Ammonium Silver Bismuthinitrite, $(\text{NH}_4)_2\text{AgBi}(\text{NO}_2)_6$.

This salt can be prepared by adding a solution of silver nitrate to a solution of ammonium nitrite containing bismuth nitrate, but as acidified solutions of ammonium nitrite are very unstable it is more convenient to add first bismuth nitrate, and then silver nitrate, to a solution of sodium nitrite in water. This mixture does not yield a precipitate of sodium-silver salt, as both these metals belong to the Y group, as previously explained. On now

adding a solution of ammonium nitrate, a red, crystalline precipitate of the ammonium-silver salt will fall.

To 25 c.c. of a 50 per cent. sodium nitrite solution are added 5 c.c. of the bismuth nitrate solution, then with constant shaking about 10 c.c. of a 10 per cent. solution of silver nitrate. The white precipitate of silver nitrite at first produced will dissolve (silver nitrite being soluble in concentrated solutions of the nitrites of the alkali metals), but there will probably remain a slight permanent precipitate of silver chloride, due to chloride almost always present in the reagents. Should this be the case, it is removed by filtration, and about 2 grams of ammonium nitrate dissolved in a very little water are added. A red, crystalline substance will be precipitated, which must be collected after a few minutes. The liquid should be kept cold throughout, and the filtration accomplished as quickly as possible. The substance is dried, as in the case of the former salts.

The substance forms fine, red crystals, apparently octahedral. It is not particularly insoluble, and the crystals can be obtained fairly large. It is quite stable at the ordinary temperature, specimens having remained unaltered after several months. Water hydrolyses it rapidly. When quite dry it explodes very feebly on being rubbed in a mortar, as also do some of the other bismuthinitrites containing ammonium.

Found: $\text{Ag}=17.2$; $\text{NH}_4=5.4$; $\text{NO}_2=43.7$.

$(\text{NH}_4)_2\text{AgBi}(\text{NO}_2)_6$ requires $\text{Ag}=17.2$; $\text{NH}_4=5.75$;
 $\text{NO}_2=43.9$ per cent.

Potassium Silver Bismuthinitrite, $\text{K}_2\text{AgBi}(\text{NO}_2)_6$.

To 30 c.c. of 50 per cent. potassium nitrite solution are added about 10 c.c. of the bismuth nitrate solution, then silver nitrate (say, 2 per cent. solution) until all chloride that may be present is precipitated, and the orange-red potassium-silver bismuthinitrite begins to fall. The mixture is filtered, and to the filtrate about 70 c.c. more of the silver nitrate solution are added gradually and with constant shaking. The salt is collected, and dried as for the other salts. By using a fairly dilute silver solution the substance is obtained in larger crystals. More concentrated solutions may be used, but in that case the salt will be precipitated in minute crystals.

The salts forms orange-red, apparently octahedral crystals. It resembles the ammonium-silver salt closely, but is less soluble. For some reason, which the authors have, so far, been unable to explain, this salt appears to be less stable than the other mixed silver bismuthinitrites. One would expect it to be much more

stable than the ammonium salt, but the reverse is the case, and the preparations hitherto made, about seven in number, have all gradually decomposed and become white on keeping, whereas preparations of the other mixed silver bismuthinitrites, made at the same time and kept under similar conditions, have remained unaltered.

Found: $\text{Ag}=16.2$; $\text{NO}_2=41.2$.

$\text{K}_2\text{AgBi}(\text{NO}_2)_6$ requires $\text{Ag}=16.1$; $\text{NO}_2=41.2$ per cent.

Rubidium Silver Bismuthinitrite, $\text{Rb}_2\text{AgBi}(\text{NO}_2)_6$.

This salt may be obtained by adding bismuth nitrate, and then silver nitrate, to a solution of rubidium nitrite (the preparation of this salt is described in the following paper, p. 2131), but the use of this salt may be avoided in the following manner. If bismuth nitrate, and then rubidium nitrate, are added to a solution of sodium nitrite, the result is the precipitation of rubidium sodium bismuthinitrite. If, however, silver nitrate be added before the rubidium salt, this precipitate will be replaced by an orange-yellow one of the rubidium-silver salt. The amount of rubidium nitrate must be limited, so that there is always enough silver present to form the rubidium-silver compound, to the exclusion of the more soluble rubidium sodium salt.

To 15 grams of pure sodium nitrite (free from potassium) water is added until the volume of the solution is about 80 c.c. To this are added about 5 c.c. of the bismuth nitrate, then gradually, and with shaking, about 15 c.c. of 10 per cent. silver nitrate solution. Should any silver chloride form, it must be filtered off. Finally, about 1 gram of rubidium nitrate dissolved in about 10 c.c. of water is added. After allowing to remain for a short time, the precipitate is collected and dried as previously described.

The salt forms orange-yellow, probably octahedral crystals. It is only very sparingly soluble, and not very rapidly hydrolysed by water.

Found: $\text{Ag}=14.2$; $\text{Rb}=22.3$; $\text{NO}_2=36.2$.

$\text{Rb}_2\text{AgBi}(\text{NO}_2)_6$ requires $\text{Ag}=14.14$; $\text{Rb}=22.4$;
 $\text{NO}_2=36.2$ per cent.

Caesium Silver Bismuthinitrite, $\text{Cs}_2\text{AgBi}(\text{NO}_2)_6$.

Although this compound is the most insoluble of all the bismuthinitrites, it is one of the most difficult to obtain in the pure state. It cannot be obtained pure by adding bismuth nitrate and silver nitrate to a solution of caesium nitrite, as when thus prepared it is contaminated with the insoluble caesium bismuthinitrite. An

attempt was made to prepare it by adding bismuth nitrate and caesium nitrate to a solution of potassium nitrite, then gradually adding silver nitrate in smaller quantity than would be required to precipitate the whole of the caesium as caesium-silver salt. It was thought that this might yield a pure product, the caesium-silver salt being formed exclusively, as it is much less soluble than the potassium-silver compound. This was not the case, as determinations of the nitrite and of the silver showed that the product contained several parts per cent. of the potassium-silver salt (Found, $\text{NO}_2 = 34.5$; $\text{Cs}_2\text{AgBi}(\text{NO}_2)_6$ requires $\text{NO}_2 = 32.2$ per cent.). Better results may be obtained by effecting the precipitation in a more dilute solution of potassium nitrite, but the most satisfactory method is to use a dilute solution of sodium nitrite, conducting the preparation as in the case of the preceding salt, rubidium-silver bismuthinitrite. Although caesium-sodium bismuthinitrite is an insoluble salt, the caesium-silver compound is still less soluble, and precipitates preferentially. The quantities to be used and the method of preparation are exactly as described for the rubidium-silver salt.

Found: $\text{NO}_2 = 32.4$.

$\text{Cs}_2\text{AgBi}(\text{NO}_2)_6$ requires $\text{NO}_2 = 32.2$ per cent.

The salt forms pale yellow, very minute crystals, which are very insoluble, and decomposed only slowly by water. It blackens slowly on exposure to light, but in absence of light appears to be stable.

Thallium Silver Bismuthinitrite, $\text{Tl}_2\text{AgBi}(\text{NO}_2)_6$.

This salt cannot readily be obtained by the addition of bismuth nitrate and silver nitrate to thallium nitrite solution, as thallium bismuthinitrite itself is an insoluble compound. It can, however, easily be prepared in a way exactly similar to that described for the rubidium-silver and caesium-silver salts, as it is very much less soluble than the thallium-sodium salt.

To 15 grams of pure sodium nitrite (free from potassium), water is added until the volume of the solution is about 60 c.c., then 5 c.c. of the bismuth nitrate solution, 15 c.c. of 10 per cent. silver nitrate solution, and a few drops of dilute acetic acid are added. The mixture is filtered, if necessary, to remove traces of silver chloride, and to the clear filtrate 20 c.c. of a 5 per cent. solution of thallium nitrate are gradually added. The red precipitate is collected after a few minutes, and dried as in the previous cases.

The salt forms a red, finely-divided, crystalline powder, which is very insoluble, and only slowly decomposed by water. It appears to be quite stable.

Found: $\text{Ag} = 10.8$; $\text{Tl} = 40.4$.

$\text{Tl}_2\text{AgBi}(\text{NO}_2)_6$ requires $\text{Ag} = 10.8$; $\text{Tl} = 40.8$ per cent.

Group C. Bismuthinitrites containing Sodium.

These are all bright yellow, crystalline salts, and they differ very much in their solubilities. The ammonium-sodium salt is very soluble, and can only be obtained from concentrated solutions; the potassium salt is extremely soluble, can only be prepared from solutions of definite concentration, and has probably not yet been obtained in a pure state; the rubidium-sodium compound is of only sparing solubility, and the caesium-sodium salt is very insoluble. The thallium salt is not particularly soluble, and can easily be prepared in the pure state.

The ammonium-sodium, rubidium-sodium, and caesium-sodium salts have, as previously mentioned, been described in earlier papers, but some further methods of preparation, etc., are included here.

Ammonium Sodium Bismuthinitrite.

As previously prepared, this salt was obtained by dissolving solid bismuth nitrate in a cold, very concentrated solution of ammonium nitrate, and pouring the resulting liquid into a cold, nearly saturated solution of sodium nitrite. Analyses of the bright yellow powder obtained pointed to the formula $(\text{NH}_4)_2\text{NaBi}(\text{NO}_2)_6$. Subsequently, it has been prepared by adding a concentrated solution of ammonium nitrate to a concentrated solution of sodium nitrite containing bismuth. In order to prepare it in this manner, about 16 grams of the nitrite are dissolved in the least possible amount of water at the ordinary temperature, 5 c.c. of the bismuth nitrate solution are added, the mixture cooled with ice, and the compound precipitated by the addition of a previously-cooled solution of 4 grams of ammonium nitrate in about 5 c.c. of water. The yellow precipitate is collected after a few minutes, and dried as previously described. It is identical in appearance with the product obtained by the former method, and under the microscope appears homogeneous. On analysis, however, the percentage of ammonium was found to be 6.04 and that of sodium 5.17. The ratio between these numbers is 1.17, and that between $3(\text{NH}_4)$ and 2Na is 1.176, pointing to the formula $9(\text{NH}_4), 6\text{Na}, 5\text{Bi}(\text{NO}_2)_6$ for the salt prepared in this way. This formula would require $\text{NH}_4 = 5.97$ and $\text{Na} = 5.07$ per cent. (compare the case of the caesium-sodium salt, given below). This and the succeeding salt can only be prepared from such concentrated solutions that it is very difficult to remove all mother liquor and ensure that a pure substance is being dealt with.

Potassium Sodium Bismuthinitrite.

This salt was at first thought to be incapable of existence, as on adding bismuth nitrate to a very concentrated solution of equal parts of the mixed nitrites of sodium and potassium, the substance deposited consisted of orange-yellow plates of potassium bismuthinitrite. It was found, however, that if a concentrated solution of potassium nitrite was gradually added to a concentrated solution of sodium nitrite containing bismuth, when a certain amount of the potassium salt had been added, bright yellow, octahedral crystals deposited, containing occasionally a few much larger, orange-coloured plates of potassium bismuthinitrite. These, if present, could be removed and a homogeneous product obtained.

To 20 grams of sodium nitrite are added 20 c.c. of water and 5 c.c. of the bismuth nitrate solution. The mixture is cooled to 0° , and any sodium nitrate that may deposit is filtered off. Into this liquid is poured a solution of 5 grams of potassium nitrite in about 5 c.c. of water, and the whole cooled to 0° . Should no precipitate form, a further small addition of potassium nitrite is made. After about half an hour the very finely-divided, yellow precipitate is collected, and as much as possible of the remaining mother liquor carefully removed by pressure on a porous plate.

The salt is a finely-divided powder, consisting of very small, bright yellow crystals, probably octahedral. The substance is unstable, and water at once hydrolyses it, although very small quantities of water produce a yellow solution.

On analysis the percentage of potassium found was 13.4, whilst the amount required by the formula $K_2NaBi(NO_2)_6$ is also 13.4. The percentage of NO_2 found was, however, much below the required quantity, being 43.6 as against 47.2. This may have been partly due to decomposition, but the formula $K_2NaBi(NO_2)_6$ can only be regarded, from these results, as probable, but not certain.

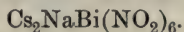
Rubidium Sodium Bismuthinitrite, $Rb_2NaBi(NO_2)_6$.

This salt has been previously described by one of the authors, and it is sufficient to mention here that it is best prepared as a bright yellow, crystalline precipitate by adding rubidium nitrate to a 15 per cent. solution of sodium nitrite containing bismuth. It is also formed in the reverse manner from rubidium nitrite by adding first bismuth nitrate, then sodium nitrite.

Caesium Sodium Bismuthinitrite.

The properties of this salt, and its use as a means of determining sodium gravimetrically, have been described by one of the present

authors in a former paper, and the salt is also referred to on p. 2112 of this paper. Like the ammonium-sodium compound, its composition appears to vary somewhat with the method of preparation. When prepared by adding a sodium salt to a solution of potassium nitrite containing bismuth and caesium, the ratio between the caesium and sodium in the salt was found to be $3\text{Cs}:2\text{Na}$, pointing to the formula $9\text{CsNO}_2, 6\text{NaNO}_2, 5\text{Bi}(\text{NO}_2)_3$, but a sample made in absence of potassium nitrite contained an amount of caesium corresponding with the normal formula:



Thallium Sodium Bismuthinitrite, $\text{Tl}_2\text{NaBi}(\text{NO}_2)_6, \text{H}_2\text{O}$.

To 25 c.c. of a 50 per cent. solution of sodium nitrite are added 5 c.c. of the bismuth nitrate solution, and then 1 or 2 grams of thallium nitrate or acetate in about 20 c.c. of water. The bright yellow crystals are collected after about an hour, and dried as previously described.

The salt forms fairly large, honey-yellow crystals, which are moderately stable on keeping, but are decomposed gradually when heated to 100° .

Found: $\text{Tl}=43.86$; $\text{Na}=2.82$; $\text{Bi}=22.36$.

$\text{Tl}_2\text{NaBi}(\text{NO}_2)_6, \text{H}_2\text{O}$ requires $\text{Tl}=43.73$; $\text{Na}=2.47$;
 $\text{Bi}=22.30$ per cent.

Another specimen, prepared in a very similar manner, did not contain any water, and was quite stable.

PART III.

Bismuthinitrites containing Nickel.

When nickel nitrate is added to solutions of the nitrites of sodium or of lithium containing bismuth, no precipitate is formed. On the addition of a salt of any of the metals of the X class a brownish-yellow or brownish-red precipitate of a mixed bismuthinitrite of the metal X and nickel is formed. These substances deposit slowly, and are micro-crystalline. They are produced with very small amounts of nickel. Owing to lack of time, these compounds were not fully investigated, but rather complex ratios were found on analysis between the metal X and nickel contained in them. Possibly this may be due to the substances consisting of mixtures of closely similar compounds containing a metal X and nickel in different ratios.

Ammonium Nickel Bismuthinitrite.

To 40 c.c. of a 50 per cent. solution of sodium nitrite are added 10 c.c. of the bismuth nitrate solution, and then to the mixture

cooled with ice a solution of 5 grams of ammonium nitrate and 2 grams of nickel nitrate in 20 c.c. of water. After a few minutes the reddish-yellow precipitate is collected and dried in the usual way.

The substance forms a yellowish-brown, micro-crystalline powder. It is very unstable, slowly evolving oxides of nitrogen, and water decomposes it immediately. It has not been possible to assign a definite formula to the substance, as the composition of different specimens varied considerably.

Found: $\text{NH}_4 = 6.05, 6.45$; $\text{Ni} = 4.16, 3.59$; $\text{Bi} = 32.9$; $\text{NO}_2 = 50.0$ per cent.

The substance also contained some water.

Potassium Nickel Bismuthinitrite.

To 40 c.c. of a 50 per cent. solution of potassium nitrite are added 5 c.c. of the bismuth nitrate solution, and then about a gram of nickel nitrate in 10 c.c. of water. Much of the precipitate deposits on the walls of the vessel. It is collected and dried in the usual manner.

This salt is a yellowish-brown, micro-crystalline powder, very similar to the nickel-ammonium salt, and, like it, very unstable.

As the salt decomposed gradually while being dried, giving off oxides of nitrogen, the value obtained for the (NO_2) is too low. The ratio between the bismuth and nickel in the salt is not affected by this decomposition. It was found to be 7.39, whereas the ratio $2\text{Bi} : \text{Ni}$ is 7.09.

Found: $\text{Ni} = 4.25$; $\text{Bi} = 31.4$; $\text{NO}_2 = 43.7$ per cent.

The compound approximates to the composition $\text{K}_4\text{Ni}, 2\text{Bi}(\text{NO}_2)_6$, plus about 6 molecules of water.

Rubidium Nickel Bismuthinitrite.

This is prepared in a similar manner to the corresponding potassium compound, nickel nitrate, and then bismuth nitrate being added to a solution of rubidium nitrite.

It is a reddish-yellow powder consisting of minute crystals, which are less soluble and much more stable than the potassium salt. As this salt could be kept for some time, it was analysed fully, and the results are, no doubt, more correct than those obtained with the two previous salts which are difficult to analyse on account of their instability.

Found: $\text{Rb} = 29.0$; $\text{Ni} = 2.75$; $\text{Bi} = 28.0$; $\text{NO}_2 = 37.14$; H_2O (by difference) = 3.11.

The formula which corresponds most nearly with these numbers is $\text{Rb}_7\text{Ni}_3\{\text{Bi}(\text{NO}_2)_6\} \cdot 4\text{H}_2\text{O}$, for the ratio of Rb to Ni from the above numbers is 10.5, whilst the atomic ratio $7\text{Rb} : \text{Ni}$ is 10.2. This formula requires $\text{Rb} = 27.4$; $\text{Ni} = 2.69$; $\text{Bi} = 28.6$; $\text{NO}_2 = 38.0$; $\text{H}_2\text{O} = 3.30$ per cent.

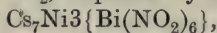
The NO_2/Bi ratio is $37.14/28.0 = 1.326$, whilst the ratio $6\text{NO}_2/\text{Bi} = 276/208 = 1.327$.

Caesium Nickel Bismuthinitrite.

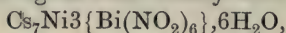
This is prepared in the same manner as the rubidium salt (the nickel nitrate must be added before the bismuth nitrate, otherwise caesium bismuthinitrite will precipitate), and resembles it closely in appearance and properties.

Found: $\text{Cs} = 36.6$; $\text{NO}_2 = 32.6$.

These figures would indicate a formula similar to that of the rubidium-nickel salt, for the ratio of Cs to $\text{NO}_2 = 36.6/32.6 = 1.12$, whilst that of 7Cs to 18NO_2 , required by the formula



is 1.12. The numbers agree most closely with the formula



which would require $\text{Cs} = 36.5$; $\text{NO}_2 = 32.5$ per cent.

Thallium Nickel Bismuthinitrite.

Fifteen grams of sodium nitrite are dissolved in about 60 c.c. of water, and 5 c.c. of the bismuth nitrate solution are added, as well as a few drops of acetic acid and 1 or 2 grams of nickel nitrate. A solution of 2 grams of thallium nitrate in about 40 c.c. of water is now added, when the substance is precipitated at once as a fine, red powder. This is collected after an hour or so, and dried as previously described.

The salt is a reddish-brown, crystalline powder, which is insoluble and decomposed slowly by water. It appears to be quite stable.

Found: $\text{Tl} = 46.54$; $\text{Ni} = 3.23$.

$\text{Tl}_4\text{Ni}_2\text{Bi}(\text{NO}_2)_6$ requires $\text{Tl} = 44.28$; $\text{Ni} = 3.13$ per cent.

Methods of Analysis.

In order to estimate the bismuth in these compounds the nitrite present was expelled by boiling with hydrochloric acid, the bismuth then precipitated with hydrogen sulphide, the sulphide dissolved in nitric acid, and the solution precipitated with ammonium carbonate, the precipitate being ignited and weighed as the trioxide.

Bismuth and silver were separated by precipitation of the silver with a slight excess of hydrochloric acid in the presence of much nitric acid.

Thallium and bismuth were separated by dissolving the salt in dilute hydrochloric or sulphuric acid, and then precipitating the bismuth as sulphide (the precipitate may contain a little thallium, which was separated by the method described by Crookes "Select Methods."). In the case of thallous silver bismuthinitrite, where the three metals are present together, the silver and bismuth were co-precipitated as sulphides from a solution in dilute sulphuric acid, and then separated by dissolving the sulphides in nitric acid (the nitric acid used in this case was more concentrated than that used for dissolution of bismuth sulphide alone, as the silver sulphide dissolved with difficulty) and precipitating the silver as chloride.

The thallium was determined generally by oxidation with decinormal permanganate, at a little below 100°, in the presence of hydrochloric acid, the thallium solution having been previously boiled with sulphurous acid to ensure the absence of thallic salts (Crookes, "Select Methods").

Thallium was also, in a few cases, determined as thallous iodide.

In the analysis of thallium nickel bismuthinitrite the salt was boiled with hydrochloric acid and much water to avoid precipitation of thallous chloride; the bismuth separated as sulphide, and the filtrate containing the nickel and thallium divided into two equal portions. To one of these was added some sulphurous acid, and the liquid boiled for some time. On titration with permanganate, 46.52 parts per cent. of thallium were found. The nickel and thallium in the other portion were separated by sodium carbonate, the thallium remaining in solution. After removal of the nickel this portion was treated exactly as the former one, and gave 46.55 per cent. of thallium. The nickel present, therefore, did not interfere with the estimation of the thallium with permanganate.

Nickel was estimated either as the dimethylglyoxime compound or as the monoxide after precipitation as peroxide. It was separated from the alkalis either by ammonium sulphide or dimethylglyoxime.

After the heavy metals had been removed by the methods indicated, caesium, rubidium, and potassium were estimated as platinum-chlorides or as sulphates, lithium as sulphate, sodium as sulphate or as sodium caesium bismuthinitrite. When two of the alkali metals were present at the same time, such as caesium and lithium, the caesium was estimated as platinichloride in one portion, and the caesium and lithium together as sulphates in another portion, the lithium being then determined by difference.

The determination of ammonium in these compounds must be made very carefully, or the results will be too low, presumably owing to interaction between the NH_4 and NO_2 groups. A weighed quantity of the substance is dropped into *cold* fairly dilute sodium

hydroxide solution, and the ammonia then distilled off in a current of steam.

Nitrite was determined by oxidation with permanganate in the following manner: Distilled water acidified with sulphuric acid so as to contain about 1 per cent. of the acid was well boiled to expel air, and then cooled to 0° . A bottle holding about half a litre was nearly filled with the cooled acidified water, and enough permanganate added to give the liquid a just perceptible pink tint. About one and a-half times the required quantity of $N/10$ -permanganate was now run into the bottle, and a weighed amount of the substance, not much greater than 0.1 gram, added in a small tube. The bottle was well shaken, and when all solid particles had disappeared, the excess of permanganate was estimated by means of a ferrous sulphate solution.

The determination has to be made with care, but gives very satisfactory results unless the compound also contains thallium, in which case, as has been previously mentioned in this paper (see p. 2117), the thallium is also partly oxidised.

The thanks of the authors are due to the Chemical Society for a grant from the Research Fund, which has defrayed the greater part of the cost of the above work, and to the managers of the Davy Faraday Research Laboratory for permission to conduct the work there.

THE DAVY-FARADAY RESEARCH LABORATORY,
ALBEMARLE ST., W.

CCXXV.—*The Nitrites of Thallium, Lithium, Caesium, and Rubidium.*

By WALTER CRAVEN BALL and HAROLD HELLING ABRAM.

THE nitrites of these metals appear to have been but incompletely examined, and as they were required in somewhat large quantities during an investigation on the bismuthinitrites, the authors thought that it would be of interest to record some points with regard to their preparation and properties.

Caesium Nitrite.

Cæsium nitrite has been prepared by G. S. Jamieson (*Amer. Chem. J.*, 1907, **38**, 616), and our preparations agreed in all

respects with his description, the salt being very soluble, hygroscopic, indistinctly crystalline, and possessing a faint yellow colour; in fact, resembling potassium nitrite very closely. Jamieson prepared the substance by the interaction of cæsium chloride and silver nitrite, and he mentions the difficulty of ensuring that this action shall be complete, unless the silver nitrite be wholly in solution. As silver nitrite is a sparingly soluble salt, a large volume of water is required, and the method is a tedious one. We discarded it in favour of the preparation from cæsium sulphate and barium nitrite, both of which are readily soluble salts. Barium nitrite can be bought in the pure state as the monohydrate $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$, and solutions of this salt and of cæsium sulphate in equivalent proportions were heated and mixed, the barium sulphate removed by filtration, and the resulting solution of cæsium nitrite evaporated. This method is less costly and troublesome, and much more rapid, than that by way of silver nitrite.

Rubidium Nitrite.

This salt does not appear to have been previously described. It was obtained both from rubidium chloride and silver nitrite, and also by the interaction of the sulphate and barium nitrite, the latter method being, for the reasons given above, the better. The salt resembles the nitrites of cæsium and potassium very closely, forming an indistinctly crystalline mass of a pale yellow tint. It is deliquescent, and very soluble in water, as 50 grams of the salt dissolved readily in about 35 c.c. of water, forming a rather viscous solution. It is only sparingly soluble in hot absolute alcohol, and almost insoluble in acetone. The addition of absolute alcohol to a concentrated aqueous solution produces at first a separation of the mixture into two layers, the heavier one containing nearly all of the salt, just as in the case of potassium nitrite. On shaking this layer with more absolute alcohol, the solid separates.

Found: $\text{Rb} = 65.2$; $\text{NO}_2 = 34.7$.

RbNO_2 requires $\text{Rb} = 65.0$; $\text{NO}_2 = 35.0$ per cent.

The salt was dried at 170° before analysis as it retained a little water when dried at 100° .

Thallous Nitrite.

This substance does not appear to have been described before. We obtained it by dissolving thallium in a mixture of nitric and sulphuric acids, the sulphuric acid being present in only slight excess of the theoretical amount required to form thallous sulphate, and the nitric acid serving to dissolve the metal more rapidly.

The liquid was then evaporated, and the solid residue heated to expel the nitric acid. The product consisted chiefly of thallous sulphate, but contained also the thallic salt. It was necessary to reduce the whole to the thallous state; otherwise, on adding barium nitrite to produce thallous nitrite, the thallic salt present would oxidise some nitrite, and a mixture of thallous nitrite and nitrate result, which could not easily be separated into its constituents. The mixture of thallous and thallic sulphate was therefore boiled with excess of sulphurous acid, and the pure thallous sulphate crystallised out. This was recrystallised, dissolved in warm water, and treated with the requisite amount of barium nitrite. After removing the barium sulphate, the pale yellow filtrate was evaporated in a vacuum over sulphuric acid, or simply on the water-bath. Evaporation over sulphuric acid is the better plan, as the product forms more distinct crystals, and there is no chance of oxidation to nitrate, which possibly occurs to a slight extent when the solution is evaporated on the water-bath.

Thallous nitrite, TlNO_2 , forms a soft, crystalline mass of a deep orange-red colour. When viewed under the microscope, the separate crystals are fairly large, but of indistinct shape, the edges generally seeming rounded; some of the crystals have the appearance of solidified drops. It melts very readily, without decomposition, to an orange-coloured liquid, and at a higher temperature evolves red fumes and leaves a pale yellow residue, probably chiefly thallous oxide, which dissolves partly in water to a strongly alkaline liquid. The salt is more soluble in water than the nitrate, for a solution was evaporated in a vacuum until it contained 27 grams per 100 c.c., and there was no sign of crystallisation. The strong aqueous solution is orange-yellow, but this colour rapidly disappears on dilution, and a dilute solution is almost colourless, the colour returning on concentration. It is insoluble in alcohol.

We did not attempt the preparation from thallous chloride and silver nitrite, as both these salts are only sparingly soluble.

The salt is anhydrous, as the following analyses show:

Found (mean of three analyses), $\text{Tl}=81.6$.

TlNO_2 requires $\text{Tl}=81.6$ per cent.

We were unable to discover a satisfactory method for the estimation of the nitrite radicle in the presence of thallium, and when the nitrite is estimated by permanganate at 0° , the thallium is also partly oxidised. The amount of oxygen taken up by the thallium is about two-thirds of that required for the oxidation to the thallic state when thallium alone is present, but rather more than this, about three-quarters, when the nitrite radicle is present also (this point is discussed further in the paper on "Bismuthi-

nitrites"). On the assumption that three-quarters of the theoretical amount of oxygen required for the complete oxidation of the thallium is taken up, then TlNO_2 would require 11.2 per cent. of its weight of oxygen for the complete oxidation of the NO_2 group plus the incomplete oxidation of the thallium. The amount found was 11.8 per cent. The formula TlNO_2 is therefore confirmed.

Lithium Nitrite.

This salt was stated by Lang to crystallise with half a molecule of water, and a formula representing this composition is given in the text-books. A short note by Rây (P., 1908, **24**, 75) states that it crystallises with one molecule of water. Our analyses confirm the formula $\text{LiNO}_2 \cdot \text{H}_2\text{O}$, and we have further examined this salt, and also anhydrous lithium nitrite. As in the case of the other nitrites described, it is more readily obtained from lithium sulphate and barium nitrite than from the chloride and silver nitrite, but we also prepared it by mixing equivalent amounts of lithium sulphate and potassium nitrite in very concentrated aqueous solution, evaporating considerably, removing by filtration the precipitate of potassium sulphate and lithium potassium sulphate, evaporating again until a dry residue was formed, and extracting this with absolute alcohol. Lithium nitrite is very soluble in absolute alcohol, whether present as LiNO_2 or as $\text{LiNO}_2 \cdot \text{H}_2\text{O}$, and as potassium nitrite is only very sparingly soluble in that solvent, the former salt is extracted in a nearly pure state. The alcoholic solution leaves, on evaporation, a white residue of small crystals, which, on the addition of a little water, changes to larger needle-shaped crystals of the monohydrate. When recrystallised once from absolute alcohol, the crystals contained only traces of potassium. The yield falls a good deal short of the theoretical, as part of the lithium is lost as potassium lithium sulphate, and, in consequence, some of the potassium nitrite is not acted on. Possibly sodium nitrite might be substituted for the potassium salt, but it would probably be more difficult to free the lithium nitrite from sodium nitrite than from potassium nitrite. Acetone might be used in place of alcohol in the above method of preparation, as it easily dissolves lithium nitrite.

The salt crystallises in flat, needle-shaped crystals, frequently 1 or 2 cm. in length. It appears to be white, having certainly less colour than the very feebly yellow-tinted sodium nitrite. It melts in its own water of crystallisation below 100° , and loses water slowly at this temperature. It is dehydrated more rapidly at 160° , losing also minute quantities of oxides of nitrogen, and leaving a residue, consisting almost entirely of the anhydrous salt, as a white

mass. It is very soluble in water, readily forming supersaturated solutions, from which crystals of $\text{LiNO}_2 \cdot \text{H}_2\text{O}$ deposit on adding a ready-formed crystal of the salt, or on cooling. A saturated solution must contain, at the ordinary temperature, about 90 grams of $\text{LiNO}_2 \cdot \text{H}_2\text{O}$ per 100 c.c., for a solution which contained 97 grams per 100 c.c. did not deposit any crystals on remaining for twenty-four hours at the ordinary temperature, but deposited approximately 6 grams per 100 c.c. after a small crystal of the salt had been added and the solution allowed to remain for some hours.

On adding a cobalt salt and a little acetic acid to a solution of lithium nitrite, a dark brown solution of lithium cobaltinitrite is formed, which, with cæsium, rubidium, potassium, and thallous salts, yields highly insoluble cobaltinitrites, just as does sodium cobaltinitrite.

The lithium nitrite used for analysis was prepared from the sulphate and barium nitrite. Before weighing, it was exposed in a desiccator over calcium chloride for about a month. Calcium chloride, therefore, does not dehydrate the salt:

0.1920 lost, on heating, 0.0493. $\text{H}_2\text{O} = 25.7$.

The dried residue, on ignition with sulphuric acid, gave
0.1471 Li_2SO_4 . $\text{Li} = 9.7$.

0.0900 required 25.2 c.c. of $N/10$ -potassium permanganate.
 $\text{NO}_2 = 64.4$.

$\text{LiNO}_2 \cdot \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 25.4$; $\text{Li} = 9.8$; $\text{NO}_2 = 64.9$ per cent.

$\text{LiNO}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ „ $\text{H}_2\text{O} = 14.6$; $\text{Li} = 11.2$; $\text{NO}_2 = 74.3$ „

The salt, dried over calcium chloride, is therefore the monohydrate.

It is interesting to note the great differences of colour between thallous nitrite and the other nitrites of the formula XNO_2 ; they all, with the possible exception of lithium nitrite, have a faint yellow tint, but thallium nitrite is deeply coloured. It appears to be the most deeply coloured of the simple nitrites of those metals which do not, as a rule, form coloured salts. Although silver, also a heavy metal, forms a nitrite of analogous composition, it is only feebly coloured. This deep colour of thallous nitrite might point to a difference from the other simple nitrites, and in this connexion one of the authors hopes to investigate the action of thallous nitrite on alkyl haloids.

Our thanks are due to the Chemical Society for a grant which defrayed part of the cost of this work, and to the Managers of the Davy-Faraday Research Laboratory, where it was carried out.

THE DAVY-FARADAY RESEARCH LABORATORY,
ALBEMARLE ST., W.

CCXXVI.—*The Catalytic Activity of Acids. Evaluation of the Activities of the Hydrogen Ion and the Undissociated Acid.*

By HARRY MEDFORTH DAWSON and FRANK POWIS.

THE view that the activity of acids in accelerating chemical change is due to the hydrogen ion rests to a large extent on the approximate proportionality between the relative catalysing powers and the corresponding values of the electrical conductivities of the acids. The velocity-coefficients used by Ostwald in making this comparison were those relating to the rate of inversion of sucrose or the rate of hydrolysis of esters.

At the time that this comparison was first instituted it was, however, recognised that the proportionality is by no means an exact one, and Ostwald supposed that the observed deviations were due to the interference of secondary factors of relatively small importance. Largely no doubt by reason of its simplicity, the theory that the catalytic activity of acids is essentially due to the hydrogen ion was accorded a most favourable reception, and for many years no serious attempt appears to have been made to challenge its validity. It is at any rate noteworthy that the efforts which were made to explain the anomalous variation of the activity of the mineral acids with concentration, and the influence of neutral salt on the activity of these acids, were not such as to bring into question the assumed relation between the velocity of the catalysed chemical change and the hydrogen-ion concentration of the catalysing acid.

In recent years the question of acid catalysis has entered into a new phase, and as a result of the accumulation of new observations and of increased accuracy in the measurement of reaction-velocities, evidence has been obtained in support of the view that the catalysing power of an acid is not entirely due to the hydrogen ion, but that the undissociated acid also contributes to the observed effect.

Observations of Acree and Johnson (*Amer. Chem. J.*, 1907, **38**, 267) on the rate of intramolecular transformation of acetylchloroaminobenzene led these authors to suggest that the catalysing acid is active in the non-ionised condition. The researches carried out by Goldschmidt on the velocity of esterification in alcoholic solution (compare *Zeitsch. physikal. Chem.*, 1910, **70**, 627; *Zeitsch. Elektrochem.*, 1911, **17**, 684; Goldschmidt and Thuesen, *Zeitsch. physikal. Chem.*, 1912, **81**, 30) have led to the expression of a similar opinion, and recent work on the rate of decomposition of methyl and ethyl diazoacetate in alcoholic solution (Bredig, Millar, and Braune,

Zeitsch. Elektrochem., 1912, **18**, 535; Snethlage, *ibid.*, p. 539) affords evidence which is distinctly favourable to the theory.

So far as aqueous solutions are concerned, the only two reactions which have been made use of in the investigation of the catalytic activity of acids and of the extent to which this varies with the acid concentration, with the temperature and pressure, and on the addition of the corresponding neutral salts, are the inversion of sucrose and the hydrolysis of esters. The latter reaction has been employed by Taylor (*Meddel. K. Vetensk. Nobelinstitut*, **2**, Nos. 34, 35, 37), whose observations relating to the influence of neutral salt and of varying concentration of the acid on the velocity of hydrolysis, are interpreted in terms of the theory that the catalytic effect is composite in character, being partly due to the hydrogen ion and partly to the undissociated acid.

If k_H denotes the catalytic activity of the hydrogen ion and k_M that of the undissociated acid, then from two experiments at different concentrations of the catalysing acid, or from two experiments with and without neutral salts in which the acid concentration is fixed, it is possible to evaluate k_H and k_M , provided that the degree of ionisation of the acid is known. The available data suffice to show that the ratio k_M/k_H varies very considerably from one acid to another, and that it decreases with the strength of the acid. In the case of the mineral acids, the ratio is greater than unity, and various observations seem to show that the activity of undissociated hydrogen chloride is about twice as great as that of the hydrogen ion. As yet, however, the accuracy attained in the evaluation of the ratio is very limited, and results obtained by different observers are not very consistent. The important question as to whether the ratio for a given acid is independent of the nature of the reaction which is catalytically accelerated has also not been answered in any satisfactory manner, although the data obtained by Taylor (*loc. cit.*) in experiments on the hydrolysis of different esters indicate that the ratio is independent of the nature of the ester.

The authors have now succeeded in obtaining experimental data which not only lend considerable support to the theory of the catalytic activity of the undissociated acid, but for the first time afford a means of determining with a fair degree of accuracy the catalysing powers of acids in the non-ionised condition.

The catalytically accelerated reaction made use of in these experiments was the isomeric transformation of acetone from the keto to the enol-form, a reaction which takes place in aqueous solution with conveniently measurable velocity at 25°, and can be readily followed in the presence of iodine, which reacts very quickly with the enolic form (Dawson and Leslie, *T.*, 1909, **95**, 1860). Under

favourable conditions the speed of this reaction is practically constant, and in this respect the isomeric transformation of the ketone possesses a distinct advantage over the two reactions (sugar inversion and ester hydrolysis) which have been mainly used in the examination of the catalysing power of acids. This constancy in the rate of disappearance of the iodine is attained if the circumstances are such that the concentration of the acetone is not appreciably altered during the progress of the reaction, and if the catalytic activity of the hydriodic acid, which is formed as one of the final products of the reaction, is negligibly small in comparison with the activity of the acid under investigation. In actual practice it is an easy matter to avoid the former source of disturbance, but the autocatalytic effect is more difficult to deal with when weak acids are under examination. In such cases the speed of the reaction increases continuously in consequence of the autocatalytic effect (compare T., 1912, **101**, 1503), and it is necessary to eliminate this in order to obtain the catalytic activity of the acid originally present in the solution. The method finally adopted to attain this end is very simple, and depends on the fact that the mean velocity of reaction during successive time intervals is a linear function of the mean concentration of the hydriodic acid which is liberated during the progress of the reaction. All that is necessary, therefore, in order to obtain the required initial velocity is to plot the observed reaction-velocities for successive time intervals as ordinates against the corresponding mean concentrations of hydriodic acid as abscissæ and extrapolate to zero concentration of hydriodic acid. An example may be given to illustrate the influence of the autocatalytic effect, and also the method by which it has been eliminated. In this experiment the catalyst employed was 0.02 molar $\alpha\beta$ -dibromopropionic acid, the concentration of the acetone 20 c.c. per litre (0.272 molar) and the original concentration of the iodine 0.00394 mol. per litre. From time to time 25 c.c. of the reaction mixture were removed to a flask containing sodium acetate in excess of the quantity of acid used as catalyst, and titrated with freshly standardised sodium thiosulphate solution of about 0.01 normality.

TABLE I.

No. of observation.	<i>t</i> (mins.).	Thiosulphate. c.c.	Iodine concentration (c). Mols. per litre.	Hydrogen iodide concentration. Mols. per litre.
1	0	21.40	0.003860	0.000080
2	100	18.74	0.003380	0.000560
3	270	14.02	0.002530	0.001410
4	430	9.29	0.001675	0.002265
5	530	6.22	0.001122	0.002818

By suitably combining these data, the following results are obtained for the connexion between the rate at which the iodine disappears and the mean concentration of the hydriodic acid.

From combin-

ation of	1 and 2.	1 and 3.	2 and 3.	2 and 4	3 and 4.	3 and 5.	4 and 5.
Mean HI concen-							
tration	0.00032	0.0375	0.0398	0.02141	0.02184	0.02211	0.02254
$-\Delta c/\Delta t \times 10^6$...	4.80	4.93	5.00	5.17	5.34	5.42	5.53

From these numbers we obtain by extrapolation an initial velocity $= 4.69 \times 10^{-6}$ mols. per litre per min., and this represents the rate of change due to the catalytic action of 0.02 molar $\alpha\beta$ -dibromopropionic acid.

In general, the acceleration due to the hydriodic acid formed increases as the ionisation-coefficient of the catalysing acid diminishes, and in the case of a given acid it increases with increasing dilution. By reducing the concentration of the iodine and increasing the quantity of the solution removed for titration, it has been found possible to determine the activity of moderately weak acids in dilute solution without difficulty.

A point to which reference should be made is the fact that all the solutions contained a certain amount of potassium iodide, the iodine being added to the reaction-mixture in the form of an iodide solution, in which the molar ratio KI/I_2 was approximately equal to 2. That the presence of potassium iodide is without measurable influence on the initial velocity of the reaction is shown by a comparison of the results obtained in experiments with monochloroacetic acid in 0.05 molar solution, in which the concentration of the potassium iodide was varied considerably. The results in question are grouped in table II.

TABLE II.

Iodine concentration, Mols. per litre.	Potassium iodide concentration. Mols. per litre.	Initial velocity.
0.004	0.008	4.55×10^{-6}
0.004	0.08	4.65×10^{-6}
0.0125	0.025	4.60×10^{-6}

The divergence of the values from the mean is probably not greater than can be accounted for on the basis of experimental error.

The results communicated in this paper have reference to the five acids—hydrochloric, dichloroacetic, $\alpha\beta$ -dibromopropionic, monochloroacetic, and acetic—which form a series of gradually decreasing strength. In the tables which follow, the concentration of the catalysing acid (c) is indicated in the first column, the degree of

ionisation (α) in the second, the hydrogen ion concentration (C_H) in the third, the initial velocity (v)* of the isomeric change in the fourth, whilst the fifth gives the ratio of the reaction-velocity to the total acid concentration, and the sixth the ratio of the velocity to the hydrogen-ion concentration. In the case of hydrochloric acid, the degree of ionisation at concentrations between 0.01 and 0.2 mol. per litre has been taken from the table given by Bray and Hunt (*J. Amer. Chem. Soc.*, 1911, **33**, 781), and that for the two more concentrated solutions from Ostwald's data, which have been reduced to the scale of Bray and Hunt's figures by comparing the two ionisation-concentration curves. For the other acids, the degree of ionisation is that calculated from the mass law by means of the ionisation-coefficients recorded in Kohlrausch and Holborn's tables.

TABLE III.

Hydrochloric Acid.

<i>c.</i>	α .	C_H .	<i>v.</i>	<i>v/c.</i>	<i>v/C_H.</i>
0.01	0.971	0.00971	4.48	448	461
0.02	0.959	0.01918	9.10	455	474
0.05	0.940	0.0470	22.9	458	487
0.1	0.921	0.0921	46.5	465	505
0.2	0.897	0.1794	95.3	476	531
0.5	0.858	0.429	243.0	486	566
1.0	0.792	0.792	515.0	515	650

Dichloroacetic Acid.

0.01	0.856	0.00356	4.10	410	479
0.02	0.769	0.0154	7.95	398	516
0.05	0.621	0.0311	18.1	362	582
0.1	0.503	0.0503	32.7	327	650
0.2	0.393	0.0786	59.6	298	758

 $\alpha\beta$ -Dibromopropionic Acid.

0.01	0.549	0.00549	2.75	275	500
0.02	0.435	0.00870	4.69	234.5	539
0.05	0.305	0.01525	8.98	179.5	589
0.1	0.2275	0.02275	14.65	146.5	644
0.2	0.167	0.0334	27.05	135	810

Monochloroacetic Acid.

0.05	0.161	0.00805	4.6	92	571
0.1	0.117	0.0117	7.6	76	650
0.2	0.0842	0.0168	11.9	59.5	708
0.5	0.0542	0.0271	23.8	47.6	878
1.0	0.0386	0.0386	40.1	40.1	1039

Acetic Acid.

0.1	0.01332	0.00133	0.72	7.2	540
0.2	0.00945	0.00189	1.20	6.0	635
0.5	0.00593	0.00299	2.07	4.14	690
1.0	0.00423	0.00423	3.35	3.35	790

* v = velocity in mols. per litre per min. $\times 10^6$.

From the values of the ratio v/C_H in the last column of the tables it is evident that in no case is there an approximation to constancy, but that for all five acids the ratio increases as the concentration increases. The observed variation indicates very definitely that the catalysing power of an acid is very far from being determined solely by the hydrogen-ion concentration of its solutions, and that in this respect there is no difference between the behaviour of strong and weak acids. On inspection of the values of the ratio of the reaction-velocity to the total acid concentration (v/c) it will be noted that this also increases with increasing concentration of the acid in the case of hydrochloric, but that it decreases with increasing concentration for the four remaining acids which have been examined.

The existence of these relations suggested that the chemical change is catalysed, not only by the hydrogen ion, but also by the non-ionised acid, and that the observed effect is the sum of the two separate effects. If c is the concentration of the catalysing acid, α its degree of ionisation, k_H and k_M the activities of the ionised and non-ionised acid, and v_H and v_M the velocities due to these components respectively, then $v_H = k_H \alpha c$ and $v_M = k_M (1 - \alpha)c$. If, further, v is the measured velocity of the reaction, then

$$v = v_H + v_M = k_H \alpha c + k_M (1 - \alpha)c,$$

and if at a different concentration c' , at which the ionisation amounts to α' , the corresponding reaction-velocities are v' , v'_H , and v'_M , then

$$v' = v'_H + v'_M = k_H \alpha' c' + k_M (1 - \alpha')c'.$$

From such a pair of equations it is possible to determine k_H and k_M , and this has been done for each of the five acids.

Apart from the varying accuracy of the experimental determination of the reaction-velocity at the different concentrations, it is apparent, from a consideration of these equations, that the most favourable conditions for the evaluation of k_H and k_M are obtained by the combination of two experiments in which the ratio of the component reaction-velocities undergoes the largest possible variation. On this account the experiments made with the highest and lowest concentrations of the catalysing acid have been utilised for the calculation of k_H and k_M in each of the five series. The values thus obtained, which are placed at the head of each of the following series of data, have then been utilised in the calculation of the reaction-velocities at the intermediate concentrations, and these numbers are recorded in the fourth column, the corresponding observed values being given in the fifth. The second and third columns give numbers which represent the component velocities due to the hydrogen ion and the undissociated acid respectively.

TABLE IV.

Hydrochloric Acid.

$k_H = 437. \quad k_M = 811.$

Concentration.	v_H .	v_M .	v .	$v_{\text{obs.}}$
0.02	8.38	0.66	9.04	9.10
0.05	20.54	2.43	23.0	22.9
0.1	40.25	6.40	46.65	46.5
0.2	78.4	16.7	95.1	95.3
0.5	187.5	57.6	245	243

Dichloroacetic Acid.

$k_H = 445. \quad k_M = 203.$

0.02	6.85	0.94	7.79	7.95
0.05	13.84	3.85	17.7	18.1
0.1	22.38	10.09	32.5	32.7

 $\alpha\beta$ -Dibromopropionic Acid.

$k_H = 440. \quad k_M = 74.$

0.02	3.83	0.84	4.67	4.69
0.05	6.71	2.57	9.3	9.0
0.1	10.01	5.72	15.7	14.65

Monochloroacetic Acid.

$k_H = 448. \quad k_M = 23.7.$

0.1	5.24	2.09	7.33	7.60
0.2	7.54	4.34	11.9	11.9
0.5	12.14	11.21	23.35	23.8

Acetic Acid.

$k_H = 425. \quad k_M = 1.55.$

0.2	0.803	0.307	1.11	1.20
0.5	1.27	0.77	2.04	2.07

In a second series of experiments with monochloroacetic acid, the concentration of the acetone was 50 c.c. per litre. If the constants obtained ($k_H = 1055$ and $k_M = 59.6$) are reduced to a concentration of 20 c.c. per litre, the values obtained are $k_H = 422$ and $k_M = 23.8$. The latter is identical with the k_M value in the tabulated series of experiments, and the k_H values are not very different. A comparison of the observed and calculated values of the reaction-velocity in the previous table shows that the two series of numbers are, on the whole, in good agreement, and it cannot be denied that substantial evidence is thereby obtained in support of the view that the catalytic activity is due to the composite influence of the ionised and non-ionised acid.

The data for the five acids afford five independent values for the activity of the hydrogen ion, which are brought together in the following table.

TABLE V.

Nature of catalysing acid.	k_H .
Hydrochloric	437
Dichloroacetic	445
$\alpha\beta$ -Dibromopropionic	440
Monochloroacetic	448
Acetic.....	425
Mean.....	439, say 440

When the magnitude of the possible experimental error which is associated with the determination of the reaction velocities is taken into consideration, it must be admitted that the agreement between the individual values is remarkably good. If the mean value $k_H=440$ is taken as representing the true activity of the hydrogen ion, it is possible to utilise all the available experimental data for the evaluation of the activities of the various acids in the non-ionised form. From each measurement of the reaction-velocity v , k_M will be obtained by means of the equation:

$$v=440ca+k_Mc(1-a).$$

The values thus deduced are collected in the following table, the particular experiment from which each number is obtained being indicated by reference to the concentration of the acid solution.

TABLE VI.

Nature of catalysing acid.	Calculated values of k_M . Mols. acid per litre.						
	0.01	0.02	0.05	0.1	0.2	0.5	1.0
Hydrochloric	725	805	740	755	795	765	800
Dichloroacetic	230	255	233	212	206	—	—
$\alpha\beta$ -Dibromopropionic	74	76	65	60	74	—	—
Monochloroacetic.....	—	—	25.2	27.7	24.6	25.1	24.1
Acetic	—	—	—	1.36	1.87	1.50	1.49

The agreement between the k_M values obtained from the experiments at different acid concentrations is as good as that which could reasonably be anticipated when the nature of the experimental data and the probable error attaching to the reaction-velocity values is taken into account.

In consequence of the greater influence of the autocatalytic effect at the higher dilutions, it is probable that the degree of trustworthiness attaching to the several k_M values increases to some extent as the concentration increases. In deducing those values which have been adopted as the most probable values of

k_M , this circumstance has been taken into account as far as possible. The values referred to are recorded in the second column of the following table; in the third column is given the value k_M/k_H or the activity of undissociated acid in terms of that of the hydrogen ion.

TABLE VII.

Acid.	k_M .	k_M/k_H .	K .
Hydrochloric	780	1.77	—
Dichloroacetic	220	0.50	5.1×10^{-2}
$\alpha\beta$ -Dibromopropionic	67	0.152	0.67×10^{-2}
Monochloroacetic	24.5	0.055	0.155×10^{-2}
Acetic	1.50	0.0034	0.0018×10^{-2}

It will be seen from the above table that the catalysing power of the undissociated acid diminishes rapidly as the ionisation tendency decreases, a relation which has already been pointed out by Snethlage (*loc. cit.*). As yet, however, it has not been possible to find any quantitative relationship between the activity of the undissociated acid and the specific affinity-coefficient, the values of which are recorded in the fourth column of the table.

It is of some interest to compare the values of k_M/k_H in the above table with those which have been calculated from observations on other catalysed reactions in aqueous solution. From Palmaer's data (*Zeitsch. physikal. Chem.*, 1897, **22**, 492) for the velocity of inversion of sucrose by hydrochloric acid at different concentrations, Snethlage has obtained $k_M/k_H = 2$. According to Taylor's observations on ester hydrolysis under the influence of hydrochloric acid (*loc. cit.*), the value of k_M/k_H is of the order 2—3. Although these numbers can only be regarded as approximate, the order of magnitude of the activity ratio is in accord with the result obtained in our experiments.

From his experiments on the rate of hydrolysis of ethyl acetate with dichloroacetic acid as catalyst, Taylor has obtained $k_M/k_H = 0.16, 0.07$, and 0.02 from three pairs of velocity-measurements. In view of the wide divergence between the three values it might be argued that the experimental results in question are opposed to the existence of a velocity-coefficient characteristic of the undissociated acid. It is, however, much more probable that the divergence is due to experimental errors on the one hand and the unsuitability of the experiments as a combination on the other. If the arithmetic mean $k_M/k_H = 0.08$ is taken as an approximate measure of the relative activity of the undissociated acid, it is seen that this value is very much smaller than that obtained by us, for according to the previous table, the activity of the undissociated dichloroacetic acid is exactly one-half that of the hydrogen ion.

A third comparison which may be made has reference to acetic

acid, for which, according to Snethlage's calculation from Arrhenius' experiments on the inversion of sucrose, $k_M/k_H = 0.006$. This is larger, but of the same order as the value obtained by us, $k_M/k_H = 0.0034$.

The question as to whether the ratio k_M/k_H is independent of the nature of the catalysed reaction has already been discussed by Snethlage and by Taylor (*loc. cit.*). According to Snethlage, the ratio is practically independent of the nature of the solvent as well as of the catalysed reaction, and is mainly determined by the magnitude of the ionisation-coefficient of the acid.* In our opinion the available experimental material is not nearly sufficient to permit of the expression of any definite opinion with regard to the connexion between k_M/k_H and the nature of the catalysed reaction. On the one hand, the values of k_M/k_H for hydrochloric and acetic acid are approximately the same, whether these are deduced from experiments on the rate of isomeric change of acetone or the velocity of sucrose hydrolysis. On the other hand, the values of k_M/k_H for dichloroacetic acid appear to differ widely according to whether the rate of isomeric change of acetone or the rate of hydrolysis of ethyl acetate is the catalysed reaction. The evidence in respect of these three reactions is therefore quite inconclusive, and for the present we are scarcely justified in assuming that the activity ratios recorded in the previous table are independent of the nature of the change which has been made use of in these experiments.

In conclusion a comparison may be made between the observed reaction-velocities and those calculated from the constants in the previous table (VII). The arrangement of the table is similar to that in table IV, except that a column is added giving the ratio of the velocity due to the non-ionised acid to that due to the hydrogen ions, that is, v_M/v_H , at each concentration.

TABLE VIII.
Hydrochloric Acid.

$k_H = 440$. $k_M = 780$.

Concentration. Mols./litre.	v_H .	v_M .	v_M/v_H .	v .	v_{obs} .
0.01	4.27	0.23	0.054	4.50	4.48
0.02	8.44	0.64	0.076	9.08	9.10
0.05	20.68	2.34	0.113	23.0	22.9
0.1	40.52	6.16	0.152	46.7	46.5
0.2	78.93	16.07	0.205	95.0	95.3
0.5	188.8	55.4	0.295	244	243
1.0	348.5	162.2	0.465	511	515

* We would point out that the ratio k_M/k_H for a given acid cannot be independent of the solvent if it is determined by the ionisation-coefficient, for the ionisation-coefficient of an acid varies with the solvent.

Dichloroacetic Acid.

$k_H = 440. \quad k_M = 220.$

0.01	3.77	0.32	0.085	4.09	4.10
0.02	6.77	1.02	0.151	7.79	7.95
0.05	13.68	4.17	0.305	17.85	18.1
0.1	22.13	10.93	0.495	33.1	32.7
0.2	34.58	26.70	0.775	61.3	59.6

 $\alpha\beta$ -Dibromopropionic Acid.

$k_H = 440. \quad k_M = 67.$

0.01	2.42	0.30	0.125	2.72	2.75
0.02	3.83	0.76	0.20	4.59	4.69
0.05	6.71	2.33	0.345	9.04	8.98
0.1	10.01	5.17	0.515	15.2	14.65
0.2	14.70	11.16	0.76	25.85	27.05

Monochloroacetic Acid.

$k_H = 440. \quad k_M = 24.5.$

0.05	3.54	1.03	0.29	4.55	4.6
0.1	5.15	2.16	0.42	7.3	7.6
0.2	7.39	4.49	0.61	11.9	11.9
0.5	11.88	11.59	0.975	23.5	23.8
1.0	16.98	23.54	1.39	40.5	40.1

Acetic Acid.

$k_H = 440. \quad k_M = 1.50.$

0.1	0.585	0.15	0.255	0.73	0.72
0.2	0.83	0.30	0.36	1.13	1.20
0.5	1.32	0.75	0.57	2.07	2.07
1.0	1.86	1.49	0.80	3.35	3.35

The degree of concordance between the calculated and observed velocities of reaction recorded in the fifth and sixth columns is convincingly in favour of the view that the catalytic action of an acid is of composite character, and that it is additively determined by the activities of the ionised and non-ionised acid.

It is of interest to compare the magnitude of the effects due to the hydrogen ion and the undissociated acid as measured by v_H and v_M . As was to be expected, the relative importance of the undissociated acid increases with increasing concentration, and one instance is afforded by the experiments in which the catalytic effect of the undissociated acid is appreciably greater than that of the hydrogen ion. This relationship is found in the case of monochloroacetic acid in *N*-solution, where $v_M/v_H = 1.39$. Assuming that the mass law is applicable to the ionisation of weak acids in more concentrated solutions, it is possible to calculate the concentration at

which the observed catalytic effect is equally shared between the hydrogen ion and the non-ionised acid. This is the case when

$$k_M c(1-a) = k_H c_a$$

that is,

$$k_M/k_H = a/(1-a).$$

The acid concentration at which the ratio $a/(1-a)$ is equal to k_M/k_H may be deduced from the ionisation-coefficient of the acid, and in this way the following values are obtained:

TABLE IX.

Dichloroacetic acid	0.31 mol. per litre.
$\alpha\beta$ -Dibromopropionic acid	0.34 ,,
Monochloroacetic acid.....	0.52 ,,
Acetic acid	1.56 ,,

It is rather surprising to find that the concentrations for which the catalytic effects of the ionised and non-ionised acids are equal should be so close together, but this becomes intelligible if the rapid fall in the activity of the non-ionised acid with its tendency to ionise is taken into consideration.

Summary.

The catalytic activity of a series of acids has been investigated by experiments on the velocity of the keto-enol transformation of acetone. The variation of the catalysing power of the several acids with concentration can be very satisfactorily interpreted on the supposition that the observed effect is due to the sum of the catalytic activities of the ionised and non-ionised acids. The activity of the non-ionised acid has been determined in terms of that of the hydrogen ion, and it is found that this diminishes rapidly as the ionising tendency of the acid decreases.

The activity ratio k_M/k_H for hydrochloric and acetic acids has approximately the same value as the ratio obtained for these acids from observations on the hydrolysis of sucrose. It cannot yet be said, however, that this ratio is independent of the nature of the catalysed reaction.

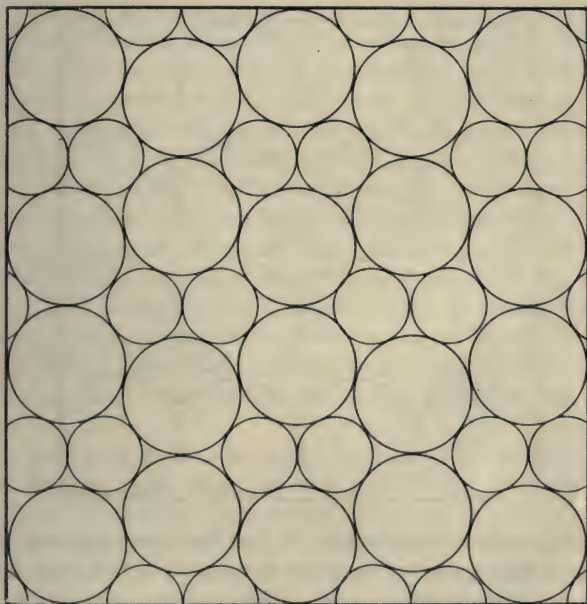
The experiments afford instances of catalysis in which the effect of the undissociated acid is equal to, and even considerably greater than, that due to the hydrogen ion.

CCXXVII.—*Contributions to the Theory of Solutions.*
The Intermiscibility of Liquids.

By JOHN HOLMES.

It has often been pointed out that current theories afford little, if any, explanation of what may be called the simpler facts associated with solution, such as relative solubility, volume changes, heat production, etc. Previous investigations in this connexion have supported the view that physical forces alone are operative in

FIG. 1.



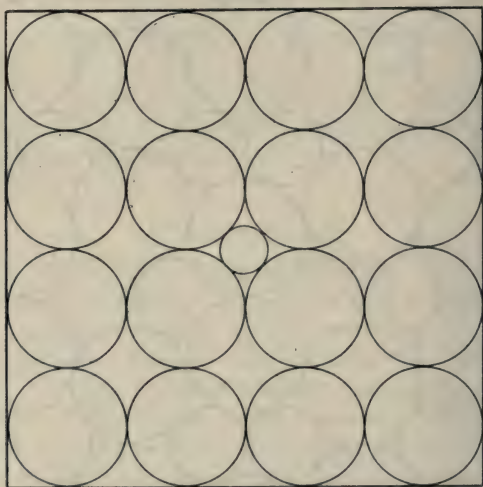
solution, and that the magnitude and extent of the accompanying phenomena are conditioned by the relative complexities of the molecules in the liquid state (T., 1906, **89**, 1781; 1907, **91**, 1608; 1909, **95**, 1919).

The liquid molecule is assumed to consist of a nucleus of great density representing the area of activity of its constituent atoms, and an outer envelope or sphere of influence, the extent of which depends on the magnitude of the resultant of electrical forces inherent in each atomic arrangement, and the consequent repulsive force between the envelopes of similar molecules.

From a purely mechanical point of view, and always assuming

absence of chemical change, any two liquids the molecular spheres of which have equal radii, should be miscible in all proportions. If, however, we have a binary mixture in which the spheres are of different sizes, then as the ratio of the radius of the larger to that of the smaller sphere increases, the dimensions of the interspaces also necessarily change, and a point is reached when the close packing of spheres is a maximum. In an equimolecular mixture this occurs when the radii are as 1.618 to 1 (Fig. 1). It is suggested that when these conditions are fulfilled the liquids are on the border line between complete as compared with partial miscibility, and that, so long as this or a smaller ratio exists, the

FIG. 2.



liquids will be mutually miscible. When, however, the ratio becomes greater than this value, a complex is formed which will not allow of the same close-packing, but results in the formation of two layers of liquid, in each of which the distribution of molecules depends on the further change in this ratio until it reaches 2.414, when, the smaller spheres being able to pass completely through the interspaces between the larger spheres (Fig. 2), the liquids should be now wholly immiscible.

The present investigation was undertaken to ascertain how closely these theoretical speculations agree with known facts.

From the curves of volume change calculated from the densities of aqueous mixtures of the lower primary alcohols it was deduced that the molecular complexity of water was the same as that of each of the alcohols (*loc. cit.*). In these circumstances the radii of the molecular spheres of methyl alcohol, ethyl alcohol, and *n*-propyl

alcohol at 15° (represented by the cube roots of the quotients of molecular weight by density) are 1.31, 1.48, and 1.60 respectively, when compared with that of water as unity. These values are well within the requirements of the above hypothesis in respect of miscibility *inter se* and with water.

The butyl alcohols, however, are only partly miscible with water, and should have molecular radii proportionately greater than those of the lower homologues, and greater also than that required theoretically for partial miscibility, namely, 1.618. Assuming similar complexity, and taking the density at 20°/4° of *isobutyl* alcohol as 0.8029 (Traube) and that of *n*-butyl alcohol as 0.8099 (Brühl), the radii of the molecular spheres compared with that of water as unity (referred to the gaseous state) are 1.723 and 1.718 respectively. Since the coefficients of expansion of liquids differ invariably, the influence of change of temperature on a binary mixture must result in corresponding differences in the dimensions of the molecular spheres, and when the ratio of the respective radii approximates to 1.62 the same initial mixture would be expected to be wholly or partly miscible according to the temperature. The solubility of water in *isobutyl* alcohol increases with rise of temperature, and an aqueous mixture containing 67.2 per cent. by weight of alcohol, corresponding with that required by the formula $C_4H_{10}O, 2H_2O$, is miscible at 113°, although at lower temperatures separation into layers occurs (Alexéev, *Ann. Phys. Chem.*, 1886, [iii], 28, 305). These facts serve, therefore, to fix the complexities of *isobutyl* alcohol as similar to those of water and the lower alcohols.

Very similar results are given by the fatty acids which from volume change considerations are also found to have a similar complexity. Compared with water, the radii of formic acid, acetic acid, propionic acid, and *n*-butyric acid are 1.28, 1.47, 1.60, and 1.72 respectively. Although *n*-butyric acid is miscible with water in all proportions at the ordinary temperature, *isobutyric* acid has only a limited miscibility. Since no data were available in respect

	(i).	(ii).	(iii).	(iv).	(v).
Weight of <i>isobutyric</i> acid ...	26.7315	18.6841	25.2368	24.6530	24.0162
Weight of water	3.9007	4.0278	5.7076	7.6157	9.3764
Density of mixture at 15°/4°	0.97303	0.97806	0.97869	0.98292	0.98607
Volume of <i>isobutyric</i> acid at 15°	28.043	19.601	26.475	25.863	25.194
Volume of water at 15°	3.904	4.031	5.713	7.622	9.384
Equivalent volume of water mixed with 100 volumes of acid at 15°	13.922	20.567	21.577	29.472	37.249
Contraction in volume when the volume of acid is constant at 100 volumes	1.662	2.095	2.155	2.535	2.837

of aqueous mixtures of the latter acid, the following mixtures were made and their relative densities determined at 15° in a pyknometer of about 25 c.c. capacity. The sample of *isobutyric acid* (Kahlbaum's) had a density 0.95323 at $15^{\circ}/4^{\circ}$ and boiling point 155.3° . Weights are reduced to vacuum.

These volume changes were plotted, and the following values obtained by interpolation:

Equimolecular Volumes at 15° (gaseous). $100\text{C}_4\text{H}_8\text{O}_2 : 19.52\text{H}_2\text{O}$.

(i). Molecular mixture.		(ii). Contraction in volume when the volume of acid is constant at 100 volumes.	(iii). Difference between the proportions by volume of acid in the initial and final volumes.
$\text{C}_4\text{H}_8\text{O}_2$.	H_2O .		
1	0.67	1.59	1.262
1	1.00	2.04	1.453
1	1.50	2.53	1.544
1	1.75	2.74	1.554
1	1.91	2.84	1.538

At lower concentrations these liquids are only partly miscible, but as seen from column iii, the difference between the proportion of *isobutyric acid* in the initial and final volumes reaches a maximum at a mixture approximating to that required by the formula $4\text{C}_4\text{H}_8\text{O}_2, 7\text{H}_2\text{O}$. According to the method adopted in previous communications for determining relative complexities, this indicates that *isobutyric acid* and water are similarly complexed. The displacement of this point from equimolecular proportions is consequent on the above theory of spheres, for in a binary mixture the point of maximum difference in volume of the constituent possessing the greater molecular volume departs more and more from an equimolecular mixture as the ratio of the radii increases from unity to 1.618 when close-packing is a maximum, and beyond which the liquids cease to be miscible—assuming that no change in radii occurs on mixing.

As in the analogous case of aqueous *isobutyl alcohol*, the solubility of water in *isobutyric acid* increases with rise of temperature, and at 7.5° there is present 71 per cent. of acid, a quantity corresponding with that required by the formula $\text{C}_4\text{H}_8\text{O}_2, 2\text{H}_2\text{O}$ (Rothmund, *Zeitsch. physikal. Chem.*, 1898, **26**, 475). Taking the density at $20^{\circ}/4^{\circ}$ of *isobutyric acid* as 0.9515, and that of *n-butyric acid* as 0.9587 (Brühl), the radii of the molecular spheres of these acids compared with that of water are 1.725 and 1.720 respectively. These values are very similar to those given above for the butyl alcohols, and the relatively greater solubility factors of the acids in water are due probably to greater contraction in volume on admixture and consequent change in radii.

These results render it probable that our hypothetical assump-

tions approximate to a true representation of the facts, and that a knowledge of density and relative solubility may suffice for ascertaining molecular complexity in the liquid state. By taking as basis the similar complexity of the homologous series of primary alcohols, fatty acids, and water, together with the fact that diminishing solubility is indicative of greater molecular volume, the determination of the complexities of other liquids would appear to present little difficulty.

Acetone.—Acetone is miscible with water in all proportions and also with the less soluble higher alcohols. According to the above theory, its molecular volume should be greater than that of water, but less than that of the butyl alcohols. The following values are calculated from McElroy's data for densities of aqueous acetone mixtures at 20° (*Amer. Chem. J.*, 1894, **16**, 618).

Equimolecular Volumes (gaseous). $100\text{C}_3\text{H}_6\text{O} : 24\cdot6\text{H}_2\text{O}$.

(i).	(ii).	(iii) ($\Delta\text{C}_3\text{H}_6\text{O}$).
$2\text{C}_3\text{H}_6\text{O}, \text{H}_2\text{O}$	-2·28	1·84
$1\frac{1}{2}\text{C}_3\text{H}_6\text{O}, \text{H}_2\text{O}$	-2·80	2·12
$\text{C}_3\text{H}_6\text{O}, \text{H}_2\text{O}$	-3·70	2·48
$\text{C}_3\text{H}_6\text{O}, 1\frac{1}{2}\text{H}_2\text{O}$	-4·96	2·74
$\text{C}_3\text{H}_6\text{O}, 2\text{H}_2\text{O}$	-5·88	2·71
$\text{C}_3\text{H}_6\text{O}, 3\text{H}_2\text{O}$	-7·03	2·42

In these and following mixtures the molecular mixture is given in column i; column ii gives the change in volume when the volume of the particular liquid in question (in this case acetone) is constant at 100 volumes, the signs + and - referring to expansion and contraction respectively; column iii refers to differences (Δ) between the proportion by volume of this liquid in the initial and final volumes.

The greatest difference between the proportion by volume of acetone before and after mixing occurs at the molecular mixture $\text{C}_3\text{H}_6\text{O}, 1\frac{1}{2}\text{H}_2\text{O}$. This result is similar to those obtained in aqueous *n*-propyl alcohol and propionic acid mixtures, and indicates that the acetone molecule is similarly complexed to that of water. The ratio of the radii of the respective molecules at 20° is therefore as 1·59 to 1.

Pyridine.—The following values are calculated from densities of aqueous mixtures of pyridine at 15·5° (Holmes, T., 1906, **89**, 1784).

Equimolecular Volumes (gaseous). $100\text{C}_5\text{H}_5\text{N} : 22\cdot5\text{H}_2\text{O}$.

(i).	(ii).	(iii) ($\Delta\text{C}_5\text{H}_5\text{N}$).
$2\text{C}_5\text{H}_5\text{N}, \text{H}_2\text{O}$	-1·12	0·91
$1\frac{1}{2}\text{C}_5\text{H}_5\text{N}, \text{H}_2\text{O}$	-1·43	1·09
$\text{C}_5\text{H}_5\text{N}, \text{H}_2\text{O}$	-1·95	1·32
$\text{C}_5\text{H}_5\text{N}, 1\frac{1}{2}\text{H}_2\text{O}$	-2·47	1·41
$\text{C}_5\text{H}_5\text{N}, 2\text{H}_2\text{O}$	-2·80	1·35
$\text{C}_5\text{H}_5\text{N}, 3\text{H}_2\text{O}$	-3·17	1·15

Here, again, ΔC_5H_5N is a maximum for the mixture $C_5H_5N, 1\frac{1}{2}H_2O$. Pyridine is miscible with water in all proportions and with most other liquids; like acetone, its molecular volume should lie between those of water and the butyl alcohols. Assuming similar complexity as indicated by the above volume-changes, the ratio of the radius of the pyridine molecule to that of water is 1.64, a value supported by the displacement of the point of greatest difference (Δ).

Nicotine.—Nicotine also is miscible with most liquids at the ordinary temperature, and the radius of its molecular sphere should approximate to that of pyridine. The following values are calculated from Pribram's data for aqueous nicotine mixtures at 20° (*Sitzungsber. K. Akad. Wiss. Wien*, 1897, iib, 106).

Equimolecular Volumes (gaseous). $100C_{10}H_{14}N_2 : 11.24H_2O$.

(i).	(ii).	(iii) ($\Delta C_{10}H_{14}N_2$).
$C_{10}H_{14}N_2, H_2O$	-1.88	1.545
$C_{10}H_{14}N_2, 1\frac{1}{2}H_2O$	-2.62	1.963
$C_{10}H_{14}N_2, 2H_2O$	-3.20	2.190
$C_{10}H_{14}N_2, 2\frac{1}{2}H_2O$	-3.70	2.322
$C_{10}H_{14}N_2, 3H_2O$	-4.17	2.407
$C_{10}H_{14}N_2, 3\frac{1}{2}H_2O$	-4.45	2.368
$C_{10}H_{14}N_2, 4H_2O$	-4.75	2.338

It is evident that these results differ materially from any obtained hitherto, inasmuch as the greatest difference between the percentage of nicotine in the initial and final volumes occurs at a mixture well removed from equimolecular proportions referred to the gaseous state. From the above figures the complexity of nicotine would appear to be one-half of that of water, and the equimolecular liquid mixture $C_{10}H_{14}N_2, 2H_2O$. As in the case of pyridine and water, the maximum difference is removed to the mixture $C_{10}H_{14}N_2, 1\frac{1}{2}(H_2O)_2$, indicating proximity to the series of liquids only partly miscible with water.

A similar complexity for nicotine is deducible from its mixtures with methyl alcohol at 20° (Winther, *Zeitsch. physikal. Chem.*, 1907, 60, 563).

Equimolecular Volumes (gaseous). $100C_{10}H_{14}N_2 : 25.14CH_4O$.

(i).	(ii).	(iii) ($\Delta C_{10}H_{14}N_2$).
$C_{10}H_{14}N_2, CH_4O$	-1.15	0.742
$C_{10}H_{14}N_2, 1\frac{1}{2}CH_4O$	-1.58	0.843
$C_{10}H_{14}N_2, 2CH_4O$	-1.93	0.866
$C_{10}H_{14}N_2, 2\frac{1}{2}CH_4O$	-2.20	0.841
$C_{10}H_{14}N_2, 3CH_4O$	-2.45	0.808

Assuming similar complexity, the ratio of the radius of the nicotine molecule to that of water as unity at 20° would be

$$\sqrt[3]{\frac{162.132}{1.00995}} \div \sqrt[3]{\frac{18.016}{0.99823}} \text{ or } 2.07.$$

If our hypothesis is correct, this value is impossible for a liquid

which is miscible with water in all proportions. By taking, however, the complexity of nicotine as one-half of that of water, the ratio of radii becomes 1.64, a value which is consistent with its relative solubility.

Below 60°, nicotine and water are miscible in all proportions, but at higher temperatures two layers separate (Hudson, *Zeitsch. physikal. Chem.*, 1904, **47**, 114). A sample of nicotine was purified and fractionated under diminished pressure, and its density determined at different temperatures in Sprengel pyknometers of 20 c.c. capacity. An aqueous mixture was prepared containing 69.23 per cent. of nicotine as required by the formula $C_{10}H_{14}N_2 \cdot 2(H_2O)_2$, or one molecule of nicotine with two molecules of water in the liquid state, and the temperature determined at which partial miscibility commenced. The mixture contained 20.4844 grams of nicotine and 9.1038 grams of water. When heated in a sealed tube it remained homogeneous until a temperature of 75.8° was reached, when a cloudiness appeared at the surface; at 76.0° this had spread through the mass of liquid, and two layers separated. Compared with water at 4°, the densities of nicotine at 26.1°, 73.3°, 74°, and 89.4° were found to be 1.0064, 0.9685, 0.96797, and 0.9552 respectively, and that of the aqueous mixture at 74° was 0.98965.

The initial volumes of nicotine and water in the mixture at 74° are 21.162 c.c. and 9.333 c.c., and the final volume 29.898 c.c., or 100 volumes of nicotine when mixed with 44.10 volumes of water contract to the extent of 2.82 volumes, so that at this temperature the volume change is still considerable (compare p. 2152).

The ratios of the radii of the nicotine and water spheres increase with rise of temperature, and at 26.1°, 73.3°, and 89.8° are 1.64, 1.65, and 1.66 respectively. These values are so close to that required theoretically for partial miscibility that they may be deemed sufficient confirmation of the complexity found above for nicotine, namely, one-half of that of water.

Ethyl Ether.—Ethyl ether is only partly miscible with water, but miscible in all proportions with the lower primary alcohols. The radius of its molecular sphere compared with that of water should lie between 1.62 and 2.41. The following values are calculated from Baker's recent data for densities of mixtures of ethyl ether with methyl alcohol at 25° (T., 1912, **101**, 411).

Equimolecular Volumes (gaseous). $100C_4H_{10}O : 38.82CH_4O$.

(i).	(ii).	(iii) ($\Delta C_4H_{10}O$).
$3C_4H_{10}O, CH_4O$	-0.74	0.53
$2C_4H_{10}O, CH_4O$	-0.99	0.70
$C_4H_{10}O, CH_4O$	-1.45	0.76
$C_4H_{10}O, 1\frac{1}{2}CH_4O$	-1.76	0.71
$C_4H_{10}O, 2CH_4O$	-1.98	0.63
$C_4H_{10}O, 3CH_4O$	-2.27	0.49

These figures indicate that ethyl ether is similarly complexed to water. The molecular volumes of these liquids at 25° are therefore as 5.80 to 1, with a corresponding ratio of radii 1.80.

Aniline.—According to Alexéev (*loc. cit.*), aniline and water are miscible in all proportions above 167°. Below this temperature they are only partly miscible, the aniline layer containing more aniline as the temperature falls. The complexity of aniline is readily determined from the curves of volume-change calculated from the densities of its mixtures with the lower alcohols.

Aniline-Ethyl Alcohol Mixtures at 16.3° (Jöbst, *Ann. Phys. Chem.*, 1883, [iii], 20, 56).

Equimolecular Volumes (gaseous). 100C₆H₇N : 62.72C₂H₆O.

(i).	(ii).	(iii) (ΔC ₆ H ₇ N).
4C ₆ H ₇ N, C ₂ H ₆ O	-0.37	0.28
2C ₆ H ₇ N, C ₂ H ₆ O	-0.71	0.41
C ₆ H ₇ N, C ₂ H ₆ O	-1.13	0.43
C ₆ H ₇ N, 2C ₂ H ₆ O	-1.48	0.29
C ₆ H ₇ N, 4C ₂ H ₆ O	-1.62	0.13

Aniline-Methyl Alcohol Mixtures at 25° (Holmes and Sageman, *T.*, 1909, 95, 1933).

Equimolecular Volumes (gaseous). 100C₆H₇N : 44.42CH₄O.

(i).	(ii).	(iii) (ΔC ₆ H ₇ N).
2C ₆ H ₇ N, CH ₄ O	-1.15	0.78
2C ₆ H ₇ N, 1½CH ₄ O	-1.57	0.89
C ₆ H ₇ N, CH ₄ O	-1.93	0.94
C ₆ H ₇ N, 1¼CH ₄ O	-2.25	0.94
C ₆ H ₇ N, 1½CH ₄ O	-2.53	0.92
C ₆ H ₇ N, 1¾CH ₄ O	-2.77	0.89
C ₆ H ₇ N, 2CH ₄ O	-2.99	0.85

These results indicate that aniline has a complexity similar to that of the primary alcohols.

Interpolating from Alexéev's curve of saturation, the critical temperature of solution for the molecular mixture C₆H₇N, 2H₂O requiring 72.1 per cent. of aniline, is 158°. The density of aniline at this temperature is calculated to be 0.9004, and that of water 0.9094. The molecular volumes, therefore, are as 5.22 to 1, and the ratio of radii 1.73.

Phenol.—At the ordinary temperature phenol is a crystalline solid melting at 42.7°, and is only partly soluble in water; at 68.5° and higher temperatures it is miscible in all proportions. Rothmund (*loc. cit.*) found that the phenol layer at 20° contained 72.2 per cent. of phenol, as required by the formula C₆H₆O, 2H₂O. The relative molecular volumes, referred to the gaseous state, are as 4.92 to 1, with a corresponding ratio of radii 1.70, a value suffi-

ciently close to the theoretical to deduce a complexity similar to that of water.

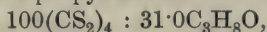
Carbon Disulphide.—Carbon disulphide is practically insoluble in water, and only partly miscible with methyl alcohol; with the higher alcohols, however, it is miscible in all proportions. The radius of its molecular sphere compared with that of water as unity would be expected to lie between 1.62 and 2.41, and to approximate more to the higher figure.

Mixtures of Carbon Disulphide with Ethyl Alcohol and with n-Propyl Alcohol at 15.5° (Holmes, T., 1906, 89, 1784).

Equimolecular Volumes (gaseous). $100\text{CS}_2 : 96.8\text{C}_2\text{H}_6\text{O}.$ }
 $100\text{CS}_2 : 124.2\text{C}_3\text{H}_8\text{O}.$ }

(i). Molecular mixture.		(ii). Expansion in volume when the volume of carbon disulphide is constant at 100 volumes in its mixtures with		(iii) (ΔCS_2). Difference between the proportions by volume of carbon disulphide in the initial and final volumes when mixed with	
CS_2 .	$\text{C}_n\text{H}_{2n+1}\text{OH}$.	ethyl alcohol.	n-propyl alcohol.	ethyl alcohol.	n-propyl alcohol.
8	1	+0.37	+0.41	0.29	0.31
6	1	+0.45	+0.50	0.33	0.34
4	1	+0.59	+0.66	0.38	0.38
3	1	+0.72	+0.78	0.41	0.39
2	1	+0.92	+0.99	0.41	0.37
1	1	+1.45	+1.44	0.37	0.28

Allowing for displacement of the point of maximum difference due to differences in radii, these results are most consistent with a quadruple complexity of carbon disulphide as compared with the alcohols. Referred to the liquid state, equimolecular volumes of carbon disulphide and n-propyl alcohol would then be



and ΔCS_2 removed to the mixture $[\text{CS}_2]_4, 1\frac{1}{4}\text{C}_3\text{H}_8\text{O}$, as in the case of aqueous ethyl alcohol mixtures, in which the equimolecular volumes are the same (p. 2165). The ratio of radii is therefore 1.48, and the liquids are mutually miscible.

Similarly, in the ethyl alcohol mixtures the molecular volumes (liquid) are $100(\text{CS}_2)_4 : 24.2\text{C}_2\text{H}_6\text{O}$, with a corresponding ratio of radii 1.61, and taking into consideration the relatively small volume change involved, the results are in agreement with the further displacement of the point of maximum difference, and also with the fact that below -14.4° these liquids have only a limited miscibility (Guthrie, *Phil. Mag.*, 1884, [v], 18, 503).

Compared with the radius of the water molecule, and accepting

quadruple complexity, that of carbon disulphide is 2.37, which compares favourably with the theoretical value (2.41) for liquids insoluble in water. Further evidence is afforded by mixtures of carbon disulphide with methyl alcohol. The critical temperature for complete miscibility of the mixture $(\text{CS}_2)_4(\text{CH}_3\text{O})_2$, representing one molecule of carbon disulphide and two molecules of methyl alcohol in the liquid state, is 40° (Rothmund, *loc. cit.*). The relative densities of the liquids at this temperature are 1.2318 and 0.7728 respectively. The molecular volumes are therefore as 5.96 : 1, with a corresponding ratio of radii 1.81.

It will be noticed that the mixing of carbon disulphide with the alcohols results in a final volume which is greater than the sum of the initial volumes, and a ratio of radii is obtained at the critical point of solution, which is greater than those observed when contraction in volume occurs.

Chloroform and Benzene.—Chloroform, like ethyl ether, is only partly miscible with water, and to a much less extent. It is miscible, however, in all proportions with methyl alcohol and its homologues. Assuming similar complexity, its molecular volume at 20° , compared with that of water, would be 4.44, and the ratio of radii 1.64. According to the present theory, this is an impossible value for a liquid so sparingly soluble in water, and if molecular volume in the liquid state be represented by the quotient of molecular weight referred to the gaseous state by density, or a simple multiple of this quantity, the molecular volume of chloroform must be at least 8.89, and greater therefore than that of ethyl ether.

On similar grounds the value 4.92 calculated for the molecular volume of benzene (referred to the gaseous state) is also highly improbable.

The following volume changes are calculated from densities of chloroform-ethyl ether mixtures at 0° (Thorpe and Rodger, T., 1897, 71, 360) and of benzene-ethyl ether mixtures at 25° (Linebarger, *Amer. Chem. J.*, 1896, 18, 429).

Chloroform-Ether Mixtures.

Equimolecular Volumes (gaseous). $100\text{CHCl}_3 : 128.60\text{C}_4\text{H}_{10}\text{O}$.

(i).	(ii).	(iii) (ΔCHCl_3).
$4\text{CHCl}_3, \text{C}_4\text{H}_{10}\text{O}$	- 0.95	0.55
$3\text{CHCl}_3, \text{C}_4\text{H}_{10}\text{O}$	- 1.22	0.60
$2\text{CHCl}_3, \text{C}_4\text{H}_{10}\text{O}$	- 1.66	0.62
$\text{CHCl}_3, \text{C}_4\text{H}_{10}\text{O}$	- 2.85	0.55
$\text{CHCl}_3, 2\text{C}_4\text{H}_{10}\text{O}$	- 4.50	0.36

*Benzene-Ether Mixtures.**Equimolecular Volumes (gaseous).* $100\text{C}_6\text{H}_6 : 116\cdot92\text{C}_4\text{H}_{10}\text{O}$.

(i).	(ii).	(iii) ($\Delta\text{C}_6\text{H}_6$).
$4\text{C}_6\text{H}_6, \text{C}_4\text{H}_{10}\text{O}$	- 0·60	0·36
$3\text{C}_6\text{H}_6, \text{C}_4\text{H}_{10}\text{O}$	- 0·75	0·39
$2\text{C}_6\text{H}_6, \text{C}_4\text{H}_{10}\text{O}$	- 1·01	0·42
$\text{C}_6\text{H}_6, \text{C}_4\text{H}_{10}\text{O}$	- 1·38	0·30
$\text{C}_6\text{H}_6, 2\text{C}_4\text{H}_{10}\text{O}$	- 1·88	0·17

From these results the complexity of ethyl ether appears to be one-half of that of chloroform or benzene. It has already been shown that carbon disulphide has a quadruple complexity compared with that of ethyl ether, and the following mixtures of carbon disulphide with benzene serve to confirm the inference that these latter liquids are complexed in the proportion of two to one respectively.

Carbon Disulphide and Benzene (Brown, T., 1881, **39**, 202).*Equimolecular Volumes (gaseous).* $100\text{CS}_2 : 147\cdot6\text{C}_6\text{H}_6$.

(i).	(ii).	(iii) (ΔCS_2).
$8\text{CS}_2, \text{C}_6\text{H}_6$	+ 0·46	0·33
$4\text{CS}_2, \text{C}_6\text{H}_6$	+ 0·76	0·40
$2\text{CS}_2, \text{C}_6\text{H}_6$	+ 1·29	0·43
$\text{CS}_2, \text{C}_6\text{H}_6$	+ 2·08	0·34
$\text{CS}_2, 2\text{C}_6\text{H}_6$	+ 2·54	0·26

The ratios of the radii of chloroform and benzene molecules compared with that of water at 20° are, therefore, 2·07 and 2·14 respectively, values which are in agreement with their known solubilities.

n-Hexane.—It is probable that every liquid when mixed with some other suitable liquid will give volume-changes sufficient in amount to determine its relative complexity. Without this check, however, speculations based on solubility relations alone must at present be deemed unsatisfactory. It might be deduced, for instance, that the homologous series of liquid paraffins was doubly complexed as compared with the alcohols (1) from their insolubility in water, and (2) from the fact that the critical temperatures for complete miscibility of mixtures of carbon disulphide with methyl alcohol, and of *n*-hexane with methyl alcohol are almost the same, namely, $40\cdot5^\circ$ and $42\cdot5^\circ$ respectively (Rothmund). Carbon disulphide and *n*-hexane should have approximately the same molecular volumes.

The molecular volume of carbon disulphide at 15° is 13·30, and that of *n*-hexane, calculated from its molecular weight (gaseous) and density, is 7·19 when compared with that of water. This figure

is inconsistent with its known insolubility in water. If, however, we double the complexity, we get a molecular volume of 14.38, which approximates so closely to that of carbon disulphide that the above deduction regarding complexity would appear to be valid. The radius of the molecular sphere of *n*-hexane would thus be 2.43, which agrees with theoretical requirements for insolubility in water.

Methyl Iodide.—The complexity of methyl iodide has already been compared with the complexities of ethyl alcohol, *n*-propyl alcohol, acetone, and ethyl acetate (T., 1909, 95, 1919). In each case the molecular volume ascertained from the curve of volume-change agrees with that required for relative solubility.

Ethyl Tartrate.—From the results of viscosity experiments it is usually assumed that the molecules of viscous liquids are highly complexed, and that the effect of solution is to break down these molecular aggregates to a simpler form. It is probable, however, that molecular complexity is not the determining factor in respect of the viscosities of liquids or of mixtures of liquids. If it be granted that a pure liquid is a collection of like spherical molecules, and the so-called molecular volume consists of an inner nucleus of great density, together with an outer sphere of influence which may differ in different liquids, an explanation of relative viscosity is to be sought rather in a comparison of the dimensions of these outer envelopes. Of these latter we have as yet little knowledge except that liquids of great molecular volume, such as the paraffins, carbon disulphide, benzene, etc., are in general less viscous than pyridine, aniline, and the lower alcohols, of which the respective molecular volumes are less in proportion (see table, p. 2164). There appears, therefore, to be no *a priori* reason why a viscous liquid should be highly complexed, and, in fact, from the point of view of the present theory, the inference is in the opposite direction, namely, that viscous liquids have small molecular volumes, and by reason of their greater number in a given space, offer proportionately greater frictional surfaces in contact with each other.

The ethyl tartrate used in this investigation was prepared by dissolving tartaric acid in ethyl alcohol, and saturating the mixture with hydrochloric acid gas at a moderately low temperature. After remaining for some days the acid and excess of alcohol were removed, and the residue mixed with from four to five times its volume of pure ethyl alcohol, and again saturated with the gas. The ethyl tartrate was finally fractionated three times at pressures varying from 200 to 500 mm. The density of the sample was found to be 1.2099 at 15°/4°, and the observed rotation in a 100 mm. tube +8.65, or $[\alpha]_D^{15} + 7.15^\circ$.

Ethyl tartrate is miscible with water and the lower alcohols in

all proportions; the radius of its molecular sphere should be greater, therefore, than that of water, but not exceed the value 1.62.

Much experimental work has been done by Patterson in connexion with changes of volume and rotation in ethyl tartrate mixtures (T., 1902, **81**, 1138 *et seq.*). In some of these mixtures, in which the volume-changes were appreciable, the highest concentration of ethyl tartrate was far removed from equimolecular proportions, and it was impossible, therefore, to construct the most important portion of the curves of volume-change. In the following mixtures of ethyl tartrate with water the densities were determined in a bottle pyknometer of about 70 c.c. capacity, weights being reduced to vacuum.

Percentage by weight of ethyl tartrate.	Density of mixture at 15°/4°.	When the volume of ethyl tartrate is constant at 100 volumes.	
		Volume of water.	Contraction in volume.
95.748	1.20568	5.377	0.571
88.392	1.19535	15.902	1.393
85.063	1.18977	21.264	1.715
80.610	1.18183	29.128	2.128
74.803	1.17110	40.755	2.677
73.811	1.16910	42.965	2.757
69.700	1.16086	52.643	3.110
65.147	1.15151	64.786	3.503
57.552	1.13526	89.316	4.137
49.019	1.11664	125.941	4.902
40.683	1.09730	176.561	5.534
30.781	1.07384	272.316	6.274
30.174	1.07240	280.223	6.327
24.024	1.05736	382.969	6.676
20.417	1.04855	472.016	6.868
13.853	1.03239	753.064	7.067
11.314	1.02615	949.212	7.101

These volume-changes were plotted, and the following values obtained by interpolation:

Equimolecular Volumes (gaseous). $100\text{C}_8\text{H}_{14}\text{O}_6 : 10.58\text{H}_2\text{O}$.

(i).	(ii).	(iii) ($\Delta\text{C}_8\text{H}_{14}\text{O}_6$).
$\text{C}_8\text{H}_{14}\text{O}_6, \text{H}_2\text{O}$	-1.02	0.842
$\text{C}_8\text{H}_{14}\text{O}_6, 2\text{H}_2\text{O}$	-1.71	1.181
$\text{C}_8\text{H}_{14}\text{O}_6, 3\text{H}_2\text{O}$	-2.26	1.325
$\text{C}_8\text{H}_{14}\text{O}_6, 4\text{H}_2\text{O}$	-2.74	1.379
$\text{C}_8\text{H}_{14}\text{O}_6, 5\text{H}_2\text{O}$	-3.12	1.362
$\text{C}_8\text{H}_{14}\text{O}_6, 6\text{H}_2\text{O}$	-3.48	1.330
$\text{C}_8\text{H}_{14}\text{O}_6, 8\text{H}_2\text{O}$	-4.02	1.205
$\text{C}_8\text{H}_{14}\text{O}_6, 12\text{H}_2\text{O}$	-4.91	0.974

The figures in column iii indicate that the complexity of ethyl tartrate is one-fourth of that of water, and if $\text{C}_8\text{H}_{14}\text{O}_6$ be taken as representing the molecular formula of ethyl tartrate in the liquid state, that of water must be $(\text{H}_2\text{O})_4$. In these circumstances the molecular volume of ethyl tartrate compared with that of water is 2.36, and the ratio of radii 1.33. This value approximates closely to that already determined for methyl alcohol, and although these liquids would appear to have nothing in common in respect of

general properties or chemical constitution, still, if the basis of our theory is correct their relative solubilities should be comparable. Ethyl tartrate was found to be almost insoluble in the higher paraffins, and like methyl alcohol miscible only partly with carbon disulphide.

A mixture of carbon disulphide and ethyl tartrate was prepared in the molecular proportion $(\text{CS}_2)_{42} \frac{1}{2} (\text{C}_8\text{H}_{14}\text{O}_6)$ —corresponding with one molecule of carbon disulphide and two molecules of ethyl tartrate in the liquid state. This mixture contained 8.1868 grams of ethyl tartrate and 24.1964 grams of carbon disulphide. The tube containing the mixture was sealed, and the temperature gradually raised in a water-bath. At temperatures below 35.9° the liquids were mutually miscible, but at 36.0° a cloudiness appeared in the lower part of the tube and spread rapidly through the mass of liquid, resulting in a separation into layers. The critical temperature of the corresponding mixture of carbon disulphide with methyl alcohol is 40° (p. 2156).

The density of carbon disulphide at $36^\circ/4^\circ$ is 1.2380, and that of ethyl tartrate 1.1890. Referred to the gaseous state the molecular volumes would be 61.50 and 173.35 respectively. Taking, however, the molecular complexities as determined above for the liquid state, namely, $(\text{CS}_2)_4$ and $\frac{1}{4}(\text{C}_8\text{H}_{14}\text{O}_6)$, the relative molecular volumes are 246.00 and 43.34, or as 5.68 to 1, with a ratio of radii 1.78. The ratio obtained for carbon disulphide-methyl alcohol was 1.81. These figures serve, therefore, to confirm the complexity of ethyl tartrate deduced from volume-change considerations.

Glycerol.—At the ordinary temperature glycerol is miscible in all proportions with water, methyl, ethyl, propyl, and butyl alcohols, but not with ethyl ether or the amyl alcohols. Its molecular sphere should approximate closely to that of water. Referred to the gaseous state, the molecular volume at 15° is 4.04 times that of water; solubility requirements would necessitate, therefore, a complexity for glycerol similar to that found for ethyl tartrate.

A sample of Kahlbaum's glycerol was fractionated in a vacuum, and the following mixtures made with ethyl tartrate:

Density of ethyl tartrate at $15^\circ/4^\circ = 1.20990$.

Density of glycerol at $15^\circ/4^\circ = 1.26396$.

Percentage by weight of ethyl tartrate.	Density of mixture at $15^\circ/4^\circ$.	When the volume of ethyl tartrate is constant at 100 volumes.	
		Volume of glycerol.	Contraction in volume.
86.833	1.22034	14.515	0.337
77.577	1.22674	27.667	0.534
68.038	1.23262	44.968	0.700
60.224	1.23693	63.222	0.804
54.263	1.24028	80.682	0.909
47.663	1.24376	105.109	1.015
42.513	1.24636	129.441	1.098
37.676	1.24869	158.345	1.170

From these figures the following values for molecular mixtures were interpolated:

Equimolecular Volumes (gaseous). $100\text{C}_8\text{H}_{14}\text{O}_6 : 42.76\text{C}_3\text{H}_8\text{O}_3$.

(i).	(ii).	(iii) ($\Delta\text{C}_8\text{H}_{14}\text{O}_6$).
$4\text{C}_8\text{H}_{14}\text{O}_6, \text{C}_3\text{H}_8\text{O}_3$	-0.27	0.22
$2\text{C}_8\text{H}_{14}\text{O}_6, \text{C}_3\text{H}_8\text{O}_3$	-0.46	0.31
$\text{C}_8\text{H}_{14}\text{O}_6, \text{C}_3\text{H}_8\text{O}_3$	-0.69	0.34
$\text{C}_8\text{H}_{14}\text{O}_6, 1\frac{1}{2}\text{C}_3\text{H}_8\text{O}_3$	-0.84	0.31
$\text{C}_8\text{H}_{14}\text{O}_6, 2\text{C}_3\text{H}_8\text{O}_3$	-0.94	0.27
$\text{C}_8\text{H}_{14}\text{O}_6, 3\text{C}_3\text{H}_8\text{O}_3$	-1.10	0.21

These results are consistent with similar complexity, and the volume occupied by the glycerol molecule is practically identical with that of water. It is probable, therefore, that the viscous nature of both ethyl tartrate and glycerol may be ascribed to their small molecular volumes as compared with molecular weights in the liquid state, and the greater frictional surfaces exposed in the jostling together of the molecules.

The following table gives the radial ratios of the molecular spheres of liquids, which, on admixture at the stated critical temperatures of solution, are on the immediate border line between complete and partial miscibility:

Mixture.	Critical temperature of solution of the molecular mixture. M_{zm} .	Ratio of molecular radii at the critical temperature.
Nicotine and water	76°	1.65
Phenol and water	20	1.70
<i>iso</i> Butyric acid and water	7.5	1.72
Aniline and water	158	1.73
<i>iso</i> Butyl alcohol and water	113	1.75
Carbon disulphide and ethyl tartrate.....	36	1.78
„ „ methyl alcohol ...	40	1.81

It will be noticed that the above ratios are somewhat greater than the theoretical (1.62). Nicotine and water give the nearest approach to this value, and they also give the greatest contractions in volume on admixture. In the other mixtures the ratios increase as the degree of contraction decreases, and reach the highest values when expansion in volume occurs. Since the mechanical close-packing of spheres must result necessarily in contraction in volume—greater, in fact, at the critical temperature than any hitherto observed—it is to be inferred that in true solution the effect of molecule on molecule is one of repulsion rather than of attraction, just as it is in a pure liquid. It has been shown in previous communications that volumetric changes resulting from the mixing of liquids can be represented, within a near approach to accuracy, by a calculable physical curve conditioned by the resultant of forces inherent in the molecules, whether contraction or expansion in volume occurs, whereas the corresponding changes obtained in mixtures in which chemical change is known to occur are to be

attributed to the physical nature and quantity of the new compounds formed, and lie on straight lines (T., 1909, 95, 1919). When, therefore, contraction occurs in solution, it is due to the fact that the change in volume resulting from close-packing is greater in magnitude than that due to the normal forces of repulsion.

Contraction in volume is usually accompanied by evolution of heat, and expansion in volume by absorption of heat. Binary mixtures are known, which afford both evolution and absorption of heat at different concentrations, as, for instance, chloroform and ethyl alcohol (Bussy and Buignet, *Ann. Chim. Phys.*, 1865, [iv], 4, 5), but there is no record of contractions and expansions in volume occurring in the same circumstances. As such behaviour was to be inferred from the present theory, a diligent search was made into the data already available, and many additional mixtures were examined with a view to obtaining information in this direction. It seemed probable that these peculiarities would occur only when the volume-changes were small, and preference was given more particularly to mixtures in which the density of one constituent was much greater than that of the other. Chloroform was mixed with methyl alcohol and also with ethyl alcohol, but contractions in volume alone were obtained. Mixtures of methyl iodide with methyl alcohol and *n*-amyl alcohol gave relatively large expansions at all concentrations. Methyl iodide mixed with ethyl ether afforded small contractions, and with chloroform small but appreciable expansions in volume. The curves of volume-change given by each pair of liquids were continuous, and had the usual character of physical curves. Mixtures of chloroform with acetone and with *n*-amyl alcohol gave the following results. The relative densities of these liquids and of their respective mixtures were determined at 25° in fine capillary pyknometers of 25 c.c. capacity, using a mercury-toluene thermostat.

Density of chloroform at 25°/25° = 1.48434.

Density of *n*-amyl alcohol at 25°/25° = 0.80915.

Density of acetone at 25°/25° = 0.78763.

Mixtures of Chloroform with n-Amyl Alcohol.

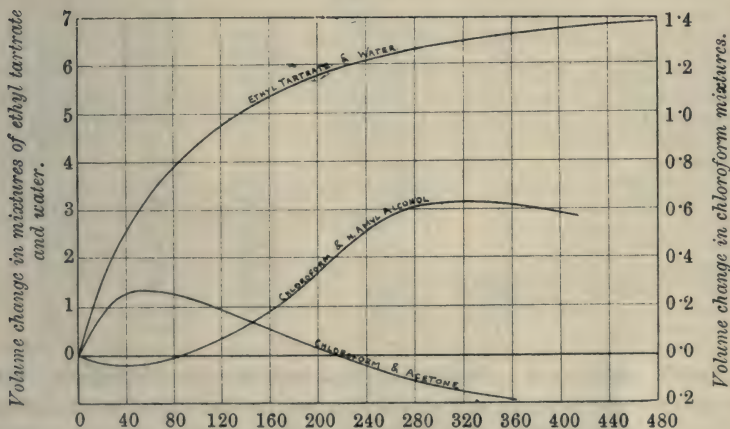
Weights in vacuum.		Density of mixture at 25°/25°.	When the volume of chloroform is constant at 100 volumes.	
Chloroform.	<i>n</i> -Amyl alcohol.		Volume of <i>n</i> -amyl alcohol.	Change in volume.
33.8719	4.2255	1.3581	22.89	+0.043
28.8802	6.9824	1.2765	44.35	+0.044
24.8772	9.0977	1.2132	67.08	+0.018
17.8526	12.9484	1.0993	133.00	-0.102
11.1636	16.6524	0.9915	273.60	-0.606
8.0171	18.1034	0.9415	414.30	-0.572

Mixtures of Chloroform with Acetone.

Weights in vacuum.		Density of mixture at 25°/25°.	When the volume of chloroform is constant at 100 volumes.	
Chloroform.	Acetone.		Volume of acetone.	Change in volume.
37·8495	2·2067	1·4165	10·99	-0·114
34·0489	4·0230	1·3594	22·26	-0·196
28·8821	6·9097	1·2700	45·08	-0·270
21·6754	10·4952	1·1532	91·23	-0·239
14·5420	14·2312	1·0327	184·40	-0·053
9·0453	17·4783	0·9373	364·07	+0·190

The volume-changes in these mixtures lie on sinuous but regular curves, showing both contractions and expansions in volume at

FIG. 3.



The base line represents volumes of water mixed with 100 volumes of ethyl tartrate, and volumes of n-amyl alcohol and of acetone mixed with 100 volumes of chloroform.

different concentrations (Fig. 3). It is difficult to see how these are to be explained, even by the elastic theory of ionic dissociation, or by any theory not acknowledging electrical affinities.

In the following table the liquids are ranged in the order of their molecular volumes as deduced from their relative complexities in the liquid state. The position of a liquid in this table decides its degree of miscibility with other liquids. Liquids adjacent to each other are miscible in all proportions, but when the ratio of the radii of the molecular spheres of any two liquids approximates to 1·7 there results a limited miscibility which becomes less in proportion to the further increase in this ratio.

Table of Molecular Complexities.

Liquid.	Temper- ature.	Complexity in the liquid state. Water = $(\text{H}_2\text{O})_4$.	Molecular volumes compared with that of water as unity at the same temperature.		Molecular radius compared with that of water
			Referred to the gaseous state.	Referred to the liquid state.	
Glycerol	15°	$\text{C}_3\text{H}_8\text{O}_3$	4·04	1·01	1·00
Formic acid	20	$(\text{CH}_2\text{O}_2)_4$	2·09	2·09	1·28
Methyl alcohol	15·5	$(\text{CH}_4\text{O})_4$	2·23	2·23	1·31
Ethyl tartrate.....	15	$\text{C}_8\text{H}_{14}\text{O}_6$	9·45	2·36	1·33
Acetic acid	15	$(\text{C}_2\text{H}_4\text{O}_2)_4$	3·17	3·17	1·47
Ethyl alcohol	15·5	$(\text{C}_2\text{H}_6\text{O})_4$	3·22	3·22	1·48
Propionic acid	25	$(\text{C}_3\text{H}_6\text{O}_2)_4$	4·06	4·06	1·60
Acetone ..	20	$(\text{C}_3\text{H}_6\text{O})_4$	4·06	4·06	1·60
<i>n</i> -Propyl alcohol ..	25	$(\text{C}_3\text{H}_8\text{O})_4$	4·16	4·16	1·60
Pyridine	15·5	$(\text{C}_5\text{H}_5\text{N})_4$	4·44	4·44	1·64
Nicotine	20	$(\text{C}_{10}\text{H}_{14}\text{N}_2)_2$	8·92	4·46	1·65
Phenol	21	$(\text{C}_6\text{H}_6\text{O})_4$	4·92	4·92	1·70
Aniline.....	25	$(\text{C}_6\text{H}_7\text{N})_4$	5·06	5·06	1·72
<i>n</i> -Butyl alcohol	20	$(\text{C}_4\text{H}_{10}\text{O})_4$	5·07	5·07	1·72
<i>n</i> -Butyric acid.....	25	$(\text{C}_4\text{H}_8\text{O}_2)_4$	5·08	5·08	1·72
<i>iso</i> Butyl alcohol	20	$(\text{C}_4\text{H}_{10}\text{O})_4$	5·12	5·12	1·72
<i>iso</i> Butyric acid	20	$(\text{C}_4\text{H}_8\text{O}_2)_4$	5·13	5·13	1·72
Ethyl acetate	25	$(\text{C}_4\text{H}_8\text{O}_2)_4$	5·47	5·47	1·76
Ethyl ether	25	$(\text{C}_4\text{H}_{10}\text{O})_4$	5·80	5·80	1·80
<i>n</i> -Amyl alcohol	20	$(\text{C}_5\text{H}_{12}\text{O})_4$	5·98	5·98	1·82
Methyl iodide	25	$(\text{CH}_3\text{I})_8$	3·49	6·98	1·91
Chloroform	20	$(\text{CHCl}_3)_8$	4·44	8·89	2·07
Ethyl iodide	20	$(\text{C}_2\text{H}_5\text{I})_8$	4·48	8·97	2·08
Benzene	20	$(\text{C}_6\text{H}_6)_8$	4·91	9·83	2·14
Carbon disulphide	15·5	$(\text{CS}_2)_{16}$	3·32	13·30	2·37
<i>n</i> -Hexane.....	17	$(\text{C}_6\text{H}_{14})_8$	7·20	14·40	2·43
<i>n</i> -Heptane	14·9	$(\text{C}_7\text{H}_{16})_8$	8·06	16·13	2·53

Much additional information is available in connexion with many of these liquids, but it only serves to confirm the conclusions already arrived at. The experimental results do not depart materially from theoretical requirements, but each helps to confirm its fellows, and no exception has been found hitherto. There is little doubt, therefore, that the intermiscibility of liquids is a function of molecular volume, and being independent of chemical constitution, offers a means of ascertaining the molecular weights of liquids comparable perhaps with those based on Avogadro's hypothesis for the gaseous state.

Although it seems improbable in view of the preceding results, the question arises as to whether the complexity of a liquid is influenced by change of temperature. The volume ratio of the molecular spheres in a binary mixture certainly varies but little with temperature, and is, in fact, proportional to differences in the expansion coefficients of the liquids. Mixtures of ethyl alcohol with water, of which the densities at different temperatures are

known more accurately than those of most liquid mixtures, afford the following values (calculated from Mendeléev's data, *Ann. Phys. Chem.*, 1869, [ii], **138**, 103, 230):

Equimolecular Volumes at 0° (gaseous). $100\text{C}_2\text{H}_6\text{O} : 31.55\text{H}_2\text{O}$.
Equimolecular Volumes at 15.5° (gaseous). $100\text{C}_2\text{H}_6\text{O} : 31.06\text{H}_2\text{O}$.
Equimolecular Volumes at 30° (gaseous). $100\text{C}_2\text{H}_6\text{O} : 30.68\text{H}_2\text{O}$.

(i).	(ii).			(iii) ($\Delta\text{C}_2\text{H}_6\text{O}$).		
	0°.	15.5°.	30°.	0°.	15.5°.	30°.
$2\text{C}_2\text{H}_6\text{O}, \text{H}_2\text{O}$	2.59	2.41	2.29	1.98	1.85	1.76
$1\frac{1}{2}\text{C}_2\text{H}_6\text{O}, \text{H}_2\text{O}$...	3.12	2.91	2.77	2.19	2.05	1.95
$\text{C}_2\text{H}_6\text{O}, \text{H}_2\text{O}$...	4.07	3.79	3.58	2.43	2.27	2.16
$\text{C}_2\text{H}_6\text{O}, 1\frac{1}{4}\text{H}_2\text{O}$...	4.71	4.34	4.10	2.51	2.33	2.21
$\text{C}_2\text{H}_6\text{O}, 1\frac{1}{2}\text{H}_2\text{O}$...	5.28	4.84	4.55	2.51	2.32	2.20
$\text{C}_2\text{H}_6\text{O}, 1\frac{3}{4}\text{H}_2\text{O}$...	5.78	5.28	4.97	2.49	2.30	2.17
$\text{C}_2\text{H}_6\text{O}, 2\text{H}_2\text{O}$	6.25	5.69	5.33	2.44	2.24	2.12

The degree of contraction varies to some extent with temperature (column ii), but the point of maximum difference between the proportion of ethyl alcohol in the initial and final volumes suffers little change (column iii, $\Delta\text{C}_2\text{H}_6\text{O}$); in other words, the relative complexity of ethyl alcohol and water is constant throughout this range.

Similar results are given by aqueous mixtures of acetic acid and pyridine at different temperatures.

Correlation of Change in Volume in Mixtures of Ethyl Alcohol and Water with Specific Refraction.

One of the most important physical constants of a liquid is its index of refraction, and just as the volume of a mixture of liquids almost invariably differs from the sum of the initial volumes, so also the corresponding index of refraction of the mixture is not additive. The index of refraction (n_D) of ethyl alcohol, for instance, is 1.36316 at 15.5°, and that of water 1.33336, but mixtures of the two give refractions far removed from the theoretical, and a mixture containing 79.2 per cent. by weight, or 84.8 per cent. by volume of alcohol has a refractive index greater even than that of either constituent, namely, 1.36661, and this is a maximum for these liquids.

In the following table the differences in refraction from the theoretical are correlated with volume-changes at the several concentrations. Columns i, ii, and iii have the same significance as in previous tables. Column iia now gives the increase in the refractive index from the theoretical, when $n_D \text{C}_2\text{H}_6\text{O}$ is 1.36316. Column iiia similarly refers to differences (Δ) between the proportion of the refractive index due to alcohol in the theoretical and observed

refractions of the mixture. Columns iv and iva refer to changes in volume and refraction when calculated as a percentage on the initial volumes and initial refractions respectively, and column v gives the refractive index of the mixture at 15.5° , as determined in this laboratory by means of the Zeiss immersion refractometer.

Equimolecular Volumes (gaseous). $100\text{C}_2\text{H}_6\text{O} : 31.06\text{H}_2\text{O}$.

$$n_{\text{D}}\text{C}_2\text{H}_6\text{O} = 1.36316 : n_{\text{D}}\text{H}_2\text{O} = 1.33336.$$

(i).	(ii).	(iia).	(iii). ($\Delta\text{C}_2\text{H}_6\text{O}$).	(iiia). ($\Delta\text{Refraction}$).	(iv).	(iva).	V.
$4\text{C}_2\text{H}_6\text{O}, \text{H}_2\text{O} \dots$	-1.45	+0.00510	1.26	0.321	1.34	0.347	1.36574
$2\text{C}_2\text{H}_6\text{O}, \text{H}_2\text{O} \dots$	2.41	0.00849	1.85	0.467	2.09	0.541	1.36651
$\text{C}_2\text{H}_6\text{O}, \text{H}_2\text{O} \dots$	3.79	0.01337	2.27	0.572	2.89	0.752	1.36630
$\text{C}_2\text{H}_6\text{O}, 1\frac{1}{2}\text{H}_2\text{O} \dots$	4.34	0.01538	2.33	0.588	3.13	0.818	1.36591
$\text{C}_2\text{H}_6\text{O}, 1\frac{1}{2}\text{H}_2\text{O} \dots$	4.84	0.01709	2.32	0.587	3.30	0.861	1.36535
$\text{C}_2\text{H}_6\text{O}, 1\frac{3}{4}\text{H}_2\text{O} \dots$	5.28	0.01858	2.30	0.576	3.42	0.890	1.36471
$\text{C}_2\text{H}_6\text{O}, 2\text{H}_2\text{O} \dots$	5.69	0.02001	2.24	0.563	3.51	0.913	1.36408
$\text{C}_2\text{H}_6\text{O}, 3\text{H}_2\text{O} \dots$	7.03	0.02459	1.95	0.489	3.64	0.944	1.36152
$\text{C}_2\text{H}_6\text{O}, 4\text{H}_2\text{O} \dots$	7.94	0.02731	1.64	0.405	3.54	0.904	1.35883
$\text{C}_2\text{H}_6\text{O}, 5\text{H}_2\text{O} \dots$	8.52	0.02939	1.35	0.337	3.34	0.856	1.35654
$\text{C}_2\text{H}_6\text{O}, 6\text{H}_2\text{O} \dots$	8.87	0.03053	1.11	0.279	3.09	0.793	1.35443
$\text{C}_2\text{H}_6\text{O}, 7\text{H}_2\text{O} \dots$	9.02	0.03095	0.92	0.231	2.84	0.726	1.35250
$\text{C}_2\text{H}_6\text{O}, 7\frac{1}{2}\text{H}_2\text{O} \dots$	9.09	0.03100	0.86	0.210	2.73	0.694	1.35162
$\text{C}_2\text{H}_6\text{O}, 8\text{H}_2\text{O} \dots$	9.08	0.03081	0.77	0.191	2.61	0.659	1.35075
$\text{C}_2\text{H}_6\text{O}, 9\text{H}_2\text{O} \dots$	9.07	0.03029	0.65	0.158	2.39	0.595	1.34919
$\text{C}_2\text{H}_6\text{O}, 10\text{H}_2\text{O} \dots$	8.99	0.02977	0.55	0.134	2.19	0.541	1.34787
$\text{C}_2\text{H}_6\text{O}, 12\text{H}_2\text{O} \dots$	8.78	0.02908	0.40	0.098	1.86	0.459	1.34581
$\text{C}_2\text{H}_6\text{O}, 20\text{H}_2\text{O} \dots$	7.88	0.02568	0.15	0.037	1.09	0.266	1.34105
$\text{C}_2\text{H}_6\text{O}, 40\text{H}_2\text{O} \dots$	6.79	0.02188	0.04	0.009	0.54	0.122	1.33721

Whether we compare columns ii and iia, iii and iiia, or iv and iva the maximum differences in refraction occur at exactly the same concentrations as the maxima for volume-change, and the observed deviation in refraction from additive relations follows so closely the change in volume that deductions proceeding from the one set of phenomena are equally relevant to the other. These results give additional support, therefore, to the hypothesis that physical forces alone are operative in solution.

In conclusion, I desire to express my indebtedness to Mr. P. J. Sageman, of this laboratory, for the experimental data relating to the above chloroform mixtures, and also to Dr. J. J. Dobbie, M.A., F.R.S., for facilities afforded me in carrying on this investigation.

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CCXXVIII.—*The Determination of Viscosity.*

By MALCOLM PERCIVAL APPLEBEY.

IN a recently-published criticism of viscosity investigations Bingham (this vol., p. 959) has raised the question of the validity and accuracy of the results obtained by the author and others with viscometers of the Ostwald type. The importance to physical chemists of a thorough and systematic examination of the laboratory methods of determining a property such as viscosity cannot easily be over-estimated. The work of Grüneisen (*Wiss. Abh. Phys.-Tech. Reichs.*, 1905, **4**, 151), fully confirmed by the author's experiments (T., 1910, **97**, 2000), by those of Merton (T., 1910, **97**, 2454), and recently by Washburn and Williams (*J. Amer. Chem. Soc.*, 1913, **25**, 737), who have effected a considerable improvement in the method of standardising viscometers, leaves little room for doubt that the determination of relative viscosity can be performed with great accuracy if sufficient care is taken in construction of the apparatus and in securing constancy of experimental conditions.

Relative and Absolute Viscosity.

Referring to the author's experiments, Bingham says (*loc. cit.*, p. 959): "It is a matter for particular regret when a research planned with the view toward the highest possible accuracy is carried out without the knowledge of conditions and corrections necessary for making the results truly absolute." In the author's opinion the question of the advisability of stating all viscosity data in absolute values is of very small importance, and simply resolves itself into a matter of convenience. In the present state of knowledge it is actually much more convenient to state accurate relative results as such, since the absolute viscosity of water cannot at present be determined with the same accuracy as the relative viscosity of a solution. The conversion of relative viscosities into absolute therefore introduces into the data an uncertainty far greater than exists in the actual determinations. The following table will make this clear:

*Average Variation from the Mean in Determinations of Viscosity by Different Viscometers.**(a) Relative Determinations.*

Observer.	No. of viscometers used.	Range of viscosity (relative).	Variation. Per cent.
Grüneisen	3	0.920—3.272	0.028
Applebey	5	1.000—3.025	0.009*
Merton	2	0.835—1.000	0.008

* Not 0.1 as stated by Bingham.

(b) Absolute Determinations.

Observer.	Variation. Per cent.
Bingham and White (<i>Zeitsch. physikal. Chem.</i> , 1912, 80, 685)	(two arms of same viscometer) 0.07.

Thus even on this basis, which does not sufficiently bring out the inaccuracy of the absolute determinations, an error is introduced eight times as large as the actual experimental error by converting the results into absolute values. If we compare the results of Bingham and White for the viscosity of water at the temperatures of the author's experiments with those of Thorpe and Rodger (*Phil. Trans.*, 1894, 185, A, 397), it will be seen that the uncertainty is actually very much greater.

Viscosity of Water.

Temperature.	Thorpe and Rodger.	Bingham and White.	Difference. Per cent.
0°	0.01778	0.01797	1.06
18	0.01062	0.01059	0.28
25	0.00891	0.008948	0.43

It should be stated, however, that the facts brought forward in this connexion are not in any sense advanced as a criticism of the work of Bingham and White. The determination of absolute viscosity is unfortunately rendered difficult by errors which can be avoided in the determination of relative viscosity, and it is not at all surprising that even careful work like that of Bingham and White should show errors and discrepancies far greater than those obtained with the simpler apparatus of Ostwald.

The Deviations from the Law of Poiseuille.

It is well known that in general the flow of liquids in capillary tubes is not strictly in accordance with Poiseuille's law:

$$\eta = \frac{\pi p r^4 t}{8 l V},$$

where η = coefficient of absolute viscosity,

p = mean pressure producing flow,

V = volume of liquid which flows through the capillary in time t ,

r = radius,

and l = length of the capillary.

The inverse proportionality between pressure and time which Poiseuille's law demands, using the same liquid at the same temperature, is only found in the case when the pressures producing flow are small and the times of flow correspondingly large.

As the time of flow diminishes, the product pt rises, and a correction factor has to be introduced into the Poiseuille expression to allow for this. Such corrections have been formulated by Neumann, Jacobsohn, Hagenbach, and Bingham and White on the assumption that the errors are due to the emergence of the liquid with a definite velocity from the end of the capillary.

On the other hand, Grüneisen has shown in a systematic study of the Ostwald viscometer that the deviations are not due to this cause, but to eddy formation at the points where there is rapid change in the character of the flow. With a well-made instrument the Poiseuille product $p \times t$ remains quite constant as t diminishes until a point of instability is reached, after which it rises rapidly, whilst the introduction of any correction of the kinetic energy type quite destroys the regularity of the results obtained. In these observations the author's work fully supports the conclusions of Grüneisen. The experiments of Merton and of Washburn and Williams (*loc. cit.*) are also completely in accord with Grüneisen's views. The last-named authors found, for a variation of the time of flow from 874.7 to 391.5 seconds, that the deviation from the mean value of $p \times t$ in no case exceeded 0.04 per cent.; if Bingham's contention were valid, a deviation of 3 per cent. would have been obtained.

It is found that the main factor in securing the efficiency of a viscometer is the character of the joins between the capillary and the reservoirs. For the preservation of the condition of stationary flow it is necessary that the joins should be even and without irregularity, and that the change of diameter should be gradual. The condition which necessarily prevails in Bingham and White's experiments, as in all absolute determinations, is extremely unfavourable to the maintenance of the correct type of flow, since the change of diameter is sudden, owing to the necessity of cutting off the capillary squarely so that its length can be measured. The flow in an absolute viscometer is probably of the type described by Bingham,* the liquid passing as a jet from the end of the capillary into the reservoir, and there expending its kinetic energy in eddies which do not resist the motion of the liquid still in the capillary to the same extent as in the case of Poiseuille motion. In an Ostwald viscometer, however, within the limits of its obedience to the law of Poiseuille, the type of flow is quite different, and eddying is entirely absent.

* The experiment quoted by Bingham, in which a long capillary was cut in pieces, is in many respects similar to Poiseuille's experiment with the tube Brv, which is considered by Grüneisen.

Constancy of Experimental Conditions.

Bingham objects to the slow flow viscometer that it is difficult to ensure constancy of conditions during the determinations. It is, of course, true that care must be exercised in the performance of accurate viscosity determinations as in any other accurate determinations. The difficulties referred to by Bingham are of three kinds:

(a) *Cleanliness.*—The vitiation of experiments by the intrusion of dust particles was, the author believes, a source of more trouble in his experiments than in those of earlier observers simply because the accuracy aimed at was higher. Very frequently experiments had to be discarded which showed in successive times of flow discrepancies which amounted only to 0.1 per cent., or even less. Such experiments would have been valid and unobjectionable if the conditions of experiment and the accuracy attainable had been of the order of those which prevail in the determination of absolute viscosity.

(b) *Constancy of Filling.*—This difficulty was specially tested for, and found to be of no account. The variation of pressure produced by the maximum variation in six fillings by a pipette was only 0.002 per cent. (*loc. cit.*, p. 2011). Washburn and Williams also arrive at 0.002 per cent. as the maximum error occasioned by this means. Bingham's suggestion of an error of 0.01 cm. in the head of liquid would mean an error of filling of 0.11 gram, which is far outside the average error of a properly used pipette.

(c) *Constancy of Temperature.*—With a Lowry spiral regulator, actuating a post-office relay through which runs the current for a heating lamp, there is no difficulty in keeping a well-stirred bath constant to 0.01° for weeks at a time, and with care the variations may be actually reduced to as little as 0.002°. The following points which the author has found to be essential for good temperature regulation will perhaps be of use to other observers.

(1) The relay contacts and the platinum-mercury contact at the top of the regulator must be kept quite clean by preventing sparking at these points. An entirely satisfactory method is to join up a condenser made of two aluminium plates immersed in tap-water across each spark-gap. The condenser used in the lamp circuit only becomes efficient after some time, usually a few hours, but after that time no spark can be seen in a dark room with a voltage of 100.

(2) Sticking of platinum and mercury must be avoided by keeping the mercury surface moving. The best way to secure this is by attaching regulator and stirrer to the same stand, an arrangement which keeps the mercury surface just trembling and

ensures rapid action. A regulator works best when it makes and breaks contact two or three times a second.

(3) It is advisable in using spiral regulators to cut a slit in the side of the cork which carries the upper contact so as to enable the pressure inside the regulator to be always equal to the external pressure. Spiral regulators respond quite considerably to differences of internal and external pressure, with the result that a regulator which is quite closed regulates at slightly different temperatures for different barometric pressures.

Gas regulation is not quite so efficient, but the variations can be quite easily kept down to 0.01° .

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CCXXIX.—*A Series of Mixtures of Nitro-compounds and Amines, which are Coloured in the Liquid State Only.*

By CHARLES KENNETH TINKLER.

SOME time ago in connexion with an investigation by the author as to the cause of the colour of certain alkyl iodides of cyclic bases, the molecular weights of these substances, in diphenylamine solution, were determined by the cryoscopic method (T., 1909, 95, 921).

The view was then put forward that the colour of some of these substances was due to polymerisation. From this investigation followed the examination of certain other substances in diphenylamine solution.

It was found that certain nitro-compounds, when dissolved in diphenylamine, give strongly-coloured solutions, but that the colour disappeared completely on solidification; thus a mixture of *p*-chloronitrobenzene and diphenylamine, which is colourless at the ordinary temperature, assumes a reddish-yellow colour at somewhat below body temperature, and loses this colour entirely when cooled.*

Again, a mixture of *p*-nitrobenzaldehyde and diphenylamine shows a deep red colour at slightly above body temperature, returning to the colourless condition when the temperature falls.

* For the demonstration of this phenomenon of colour-change the mixture is conveniently contained in a thin layer between two test-tubes placed one inside the other.

*A large number of other nitro-compounds, such as *o*- and *m*-chloronitrobenzene, *p*-bromo- and iodo-nitrobenzenes, *m*-nitrobenzaldehyde, *m*-nitrobenzonitrile, *p*-nitrotoluene, *m*- and *p*-nitrobenzoic acids, etc., also show the phenomenon to varying extents. Other amines, such as *p*-toluidine, tribenzylamine, or triphenylamine, may be substituted for the diphenylamine in some cases.

As is well known, mixtures of amines and nitro-compounds, such as trinitrobenzene and picryl chloride, often give rise to permanently coloured compounds (Hepp, *Annalen*, 1882, **215**, 344; Sudborough, T., 1901, **79**, 572; 1902, **81**, 507, etc.; Noeltling and Somerhoff, *Ber.*, 1906, **39**, 76, and others), whilst other investigators have observed the production of coloured solutions by dissolving amines in tetranitromethane (Ostomisslensky, *Ber.*, 1910, **43**, 197; A. Werner, *Ber.*, 1909, **42**, 4324); thus diphenylamine and trinitrobenzene give a strongly-coloured compound, produced by the combination of one molecule of amine and two of nitro-compound. No change in colour is produced on cooling this substance.

It is of interest to note that an aromatic nitro-compound is not necessary for this phenomenon of colour change; thus on the addition of tetranitromethane to solid diphenylamine a very dark brown coloration is produced, which is entirely removed when the mixture is cooled in ice and salt. After repeating this last experiment several times a permanent green coloration is produced, probably owing to the decomposition of the nitro-compound. In the case of the mixture of *p*-chloronitrobenzene and diphenylamine, however, a tube filled with the mixture five years ago shows the phenomenon as well now as when first prepared.

The temperature necessary to produce the colour in any given mixture depends simply on the melting points of the constituents of the mixture, or rather, as will be shown later, on the eutectic temperature of the mixture, and whenever colour is produced, part at least of the mixture is in the liquid state. The phenomenon depends on a change of state rather than on a change of temperature.

The action of solvents on the mixtures under review leads to the production of colour in very concentrated solution, but the colour is easily removed on dilution; thus a concentrated solution of *o*-chloronitrobenzene and diphenylamine in benzene rapidly becomes colourless on dilution, more readily, however, on dilution with alcohol than with benzene. Again, on mixing dilute solutions of the nitro-compound and amine, no colour is produced. This is in agreement with the behaviour of some of the additive compounds of trinitrobenzene and amines which are decomposed by solvents (compare Sudborough, *loc. cit.*).

On attempting to precipitate the coloured substance by the addition of water to a concentrated alcoholic solution of one of the mixtures, a red substance is produced, and at first sight it would appear that a compound of nitro-derivative and amine was obtained, which existed in the solid state. On closer investigation, however, it is found that the colour is due to the fact that the mixture is supercooled, as when the mixture is completely solidified, by agitation, the colour entirely disappears. A suitable mixture for the demonstration of this phenomenon is one of diphenylamine containing about one-third of its weight of *p*-nitro-benzaldehyde.

On subjecting some of these mixtures to fractional distillation it is found, as would be expected, that the constituent of lower boiling point is present in excess in the first portion of the distillate, and that the phenomenon of colour change is shown to a varying extent with each portion of the distillate.

Attempted Explanation of the Phenomenon.

In looking for an explanation of the phenomenon of colour change on heating and cooling, it has to be borne in mind that strongly-coloured compounds of amines and nitro-derivatives, such as trinitrobenzene, previously referred to, are well known substances, although, as will be shown later, no evidence of compound-formation has so far been obtained in the mixtures under review. Also, the presence of a nitro- and amino-group in the same molecule often gives rise to intense colorations, as, for example, in the nitroanilines.

Various formulæ have been suggested for the compounds of amine and nitro-derivative where such compounds have been isolated, and, as in the case of the nitroanilines, a quinonoid constitution has been assigned to them by some investigators on account of their colour.

A quinonoid constitution, however, does not appear to be necessary for the substances under review, since the aliphatic nitro-compound, tetranitromethane, may be used as the nitro-compound in the mixture. Similarly, an aromatic amine is not necessary for the production of a colour with a nitro-compound. Many nitro-compounds, such as di- and tri-nitrobenzenes, give strongly-coloured solutions in liquid ammonia, and a red additive compound of ammonia and trinitrobenzene has previously been described (Korczyński, *Bull. Acad. Sci. Cracow*, 1908, 333).

Finally, tetranitromethane and liquid ammonia give an orange-yellow solution, which by its own evaporation produces a yellow solid, and A. Werner (*loc. cit.*) has previously observed that tetranitromethane and trimethylamine give a strongly-coloured solution.

In these cases, however, the possibility of the formation of the coloured modification of nitroform has to be taken into account.

The change from colourless to coloured and vice versa in these mixtures is doubtless due to some change in the configuration of the nitro-group, as in the case of nitrogen peroxide, N_2O_4 , and nitrogen dioxide, NO_2 ; in fact, the production of a white solid, by the freezing of one of these coloured mixtures, shows a striking resemblance to the production of a white solid by freezing the coloured liquid nitrogen peroxide.

The colour-change is also doubtless connected with the residual affinity of the amine. For just as the strongly-coloured nitro-anilines give colourless solutions in concentrated hydrochloric acid, so the substitution of bromine or chlorine for hydrogen in the diphenylamine disturbs the distribution of the residual affinity of the amine, and tetrachloro- and tetrabromo-diphenylamine do not give these colour reactions with nitro-compounds.

Baly, Tuck, and Marsden (T., 1910, **97**, 571) point out that in the case of certain nitro-compounds, such as nitroquinol dimethyl ether, α -nitronaphthalene, and 4-nitro-*o*-xylene, an increase in the residual affinity of the solvent causes a shift in the absorption band towards the red end of the spectrum. It is possible, therefore, that the phenomena observed when nitro-compounds are dissolved in diphenylamine is an extreme case of this process of colour intensification.

According to Hantzsch (*Ber.*, 1912, **45**, 85), it is necessary to distinguish between three kinds of nitro-group attached to carbon.

(1) The true nitro-group, $:C \cdot N \begin{smallmatrix} \nearrow O \\ \searrow O \end{smallmatrix}$ or $:C \cdot N < \begin{smallmatrix} O \\ | \end{smallmatrix}$, present in nitro-compounds, such as nitromethane;

(2) the *ac*initro-group, $:C \cdot \begin{smallmatrix} N \\ | \\ O \end{smallmatrix} \cdot O \cdot M$ or $:C \cdot N \cdot O \cdot OM$, present in the

salts of nitro-compounds;

and (3) the conjugated *ac*initro-group, $\begin{array}{c} \text{X} \cdots \\ | \\ \cdot C \cdot N \cdot O \cdot M \\ | \\ O \end{array}$ or $\begin{array}{c} \text{X} \cdots \\ | \\ \cdot C \cdot N \cdot O \cdot O \cdot M \\ | \\ O \end{array}$,

where the nitro-group is associated in the same molecule with an electronegative group X (NO_2 , NOH , CO_2H , CN , etc.), to which it is united by subsidiary valency through the metal, alkyl radicle, or hydrogen directly attached to the nitro-group.

The absorption due to the first two types does not fall in the visible region of the spectrum, but the third type is characterised by strong absorption, which extends into the visible region of the spectrum.

It is possible that the colour in some of the mixtures under review might be due to a change in the configuration of the nitro-group similar to the formation of a conjugated *ac*initro-group, but

this hypothesis would not explain the colours of mixtures containing tetranitromethane. In the case of this substance it is impossible to write an ordinary conjugated *ac*initro-group, as none of the nitro-groups can be attached to carbon by a double bond.

The permanent colour production observed in solution with tetranitromethane and various substances having residual affinity, first noticed by Ostromisslensky and also by A. Werner (*loc. cit.*), is being investigated by Clarke, Macbeth, and Stewart by means of the spectrograph (P., 1913, **29**, 161). Since it is probable that the permanent colours produced in these cases are due to a cause similar to that which produces the transient colours in the mixtures referred to in the present paper, the question as to the cause of this colour will again be dealt with in a later communication. At present it appears possible that the attraction between the amine and the nitro-group causes a distribution of residual affinity in the latter, which approximates more or less to that in the dissociated form of nitrogen peroxide, $\begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}$.

Physico-chemical Investigations of the Mixtures.

Various physico-chemical investigations have been undertaken in order to detect, if possible, the formation of a compound between the amine and nitro-derivative in these mixtures.

The first method tried was the determination of melting-point curves for the mixtures, which is the usual method for the detection of such combinations. In these mixtures, however, no evidence of any compound formation was obtained by this method. In the cases investigated all the curves obtained showed a eutectic, and were V-shaped. No W-shaped curve was obtained.

In order to obtain a W-shaped curve it would appear to be necessary that the compound should separate in the solid state, but this is not the case in these mixtures, or they would remain coloured on cooling or precipitation from solution.

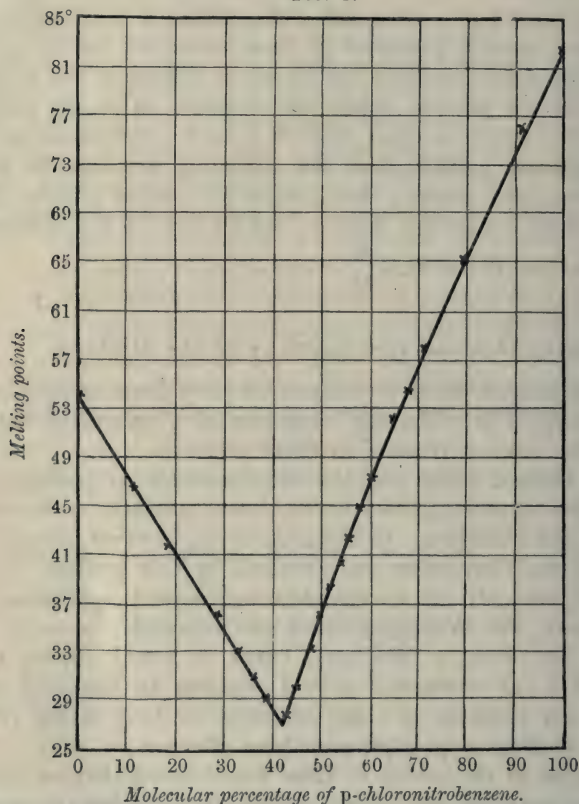
It was found in the course of these experiments that on heating up a given mixture, as soon as the temperature reaches the eutectic temperature the colour begins to develop, that is, the colour is dependent on the presence of liquid. It is also noticed that when a mixture is completely liquefied it has developed its maximum colour.

The melting-point curve for mixtures of *p*-chloronitrobenzene and diphenylamine is shown in Fig. 1. The eutectic temperature of the mixture is 27°, and the eutectic mixture contains 42·5 molecular percentage of the nitro-derivative. On heating the various mixtures of these two substances the colour commences to develop at 27°. If, however, a mixture contains a very large percentage

of the nitro-derivative, the colour begins to develop at a slightly lower temperature.

Spectroscopic investigation, which has been limited to dilute solutions of mixtures containing aromatic nitro-compounds, has so far failed to throw any light on the subject. No visible colour is produced by mixing dilute solutions of the constituents of a mixture, and the ultra-violet absorption produced by a certain

FIG. 1.



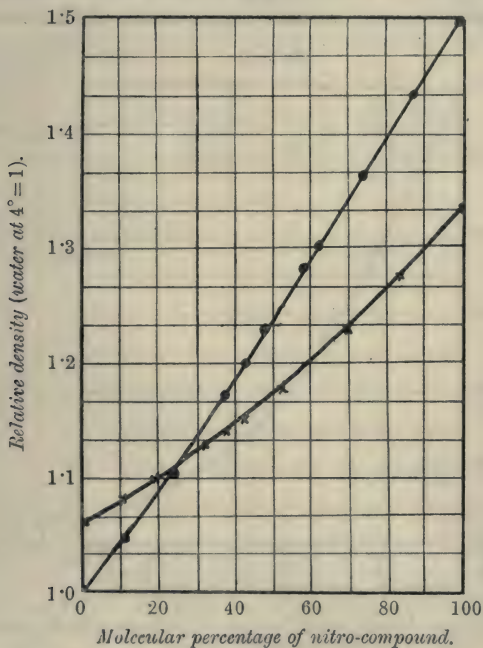
Melting-point curve of mixtures of diphenylamine and p-chloronitrobenzene.

thickness of layer is identical with that produced by layers half the thickness of the constituent solutions taken side by side, showing that in dilute solution the amine and nitro-compound are without action on one another.*

* Since this paper was written, it appears from some preliminary experiments that with very concentrated solutions it is possible to determine spectroscopically the proportions in which the substances exert maximum effect, as to colour production, on one another (compare Ostromisslensky, *Ber.*, 1911, 44, 268).

A series of density determinations of the fused mixtures was undertaken, both in the case of one of these mixtures showing the phenomenon of colour change, and in the case of permanent compound formation. The diagram, Fig. 2, shows the results obtained. In both cases very little deviation from a straight line is observed. The determinations were carried out at 60° and 130° respectively. The method employed was that of weighing a sphere of known volume in the mixture kept at the required temperature by means of a thermostat.

FIG. 2.



Relative densities of mixtures of:

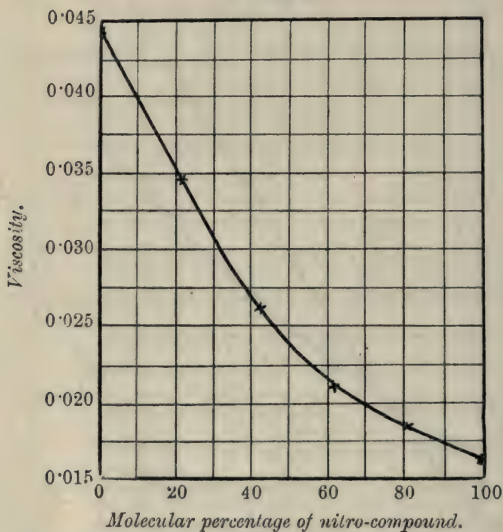
- I. Diphenylamine and o-chloronitrobenzene at 60° — x — x —
 II. „ „ trinitrobenzene at 130° — . . . —

Experiments were carried out to ascertain if any rise of temperature occurred on mixing the fused constituents of the mixtures under review. In no case was a rise of more than 0.4° observed, even when 10 grams of one of the constituents were mixed with 5 grams of the other. This, however, does not afford evidence of non-compound formation, as in the case where a compound is formed in the solid state, for example, with diphenylamine and trinitrobenzene, on mixing 8 grams of the former with 2½ grams of the latter, both at 138°, a rise of only 0.4° was observed.

Viscosity measurements were made on mixtures of *o*-chloronitrobenzene and diphenylamine, but as will be seen from the diagram, Fig. 3, no definite conclusion as to the formation of a compound can be drawn from this result.

It is possible that none of these methods is sufficiently accurate to detect the formation of a small amount of compound which might give rise to the colour. Other physico-chemical determinations remain to be carried out, but so far only from analogy to the compounds of amines and nitro-derivatives, which can be obtained in the solid state, can it be said that when in the coloured condition the mixtures under review contain compounds of the two constitu-

FIG. 3.



Viscosities in absolute units of mixtures of diphenylamine and o-chloronitrobenzene at 60°.

ents These compounds, if formed, must, however, be very unstable, since the cohesion of one or both of the constituents in the solid state is sufficient to overcome the molecular attraction of the one substance for the other. On the other hand, the presence of the amine in the fused state may be sufficient to cause the nitro-compound to assume a constitution, which gives rise to the colour, without any chemical combination taking place between the two substances.

The investigation is being extended to mixtures of nitro-derivatives and phenols and nitro-derivatives and hydrocarbons. As is well known, certain nitrophenols are coloured substances, and others give rise to coloured salts. Sudborough and Beard (T., 1911, 99,

209) have prepared a large series of coloured additive compounds of nitro-derivatives, such as trinitrobenzene, and certain phenols. Coloured compounds of nitro-derivatives and hydrocarbons are also, of course, well known.

Certain of the nitro-compounds mentioned in this paper, especially tetranitromethane, when mixed with phenols, such as thymol or α -naphthol, and with certain hydrocarbons, such as naphthalene, give strongly-coloured mixtures, from which the colour is entirely removed by cooling in a freezing mixture. Similar phenomena are also shown by certain mixtures of ketones and diphenylamine; thus a mixture of anthraquinone and diphenylamine develops an intense coloration on heating, which is lost on solidification and precipitation from solution.

The investigation will therefore be extended to include these substances, and also to certain mixtures containing iodine compounds.

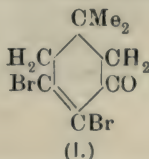
THE UNIVERSITY, EDGBASTON,
BIRMINGHAM.

CCXXX.—*Derivatives of o-Xylene. Part VI.* *5-Bromo-o-3-xylenol.*

By ARTHUR WILLIAM CROSSLEY.

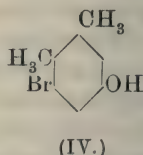
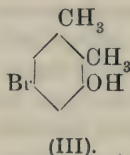
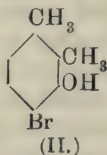
IN 1903 (T., **83**, 128) the present author, in conjunction with Le Sueur, showed that under certain conditions phosphorus pentabromide acted on dimethyldihydroresorcin to give a monobromoxyleneol, melting at 84° . At that time the only point definitely established about its constitution was that it gave tribromo-*o*-3-xylenol on treatment with bromine, and that it was therefore a monobromo-*o*-3-xylenol.

More recently this same bromoxyleneol has been obtained by the action of (a) heat, (b) potassium hydroxide on dibromodimethylcyclohexenone (I), a substance the constitution of which has been



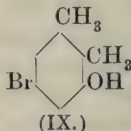
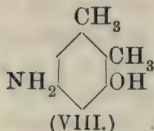
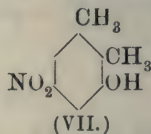
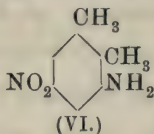
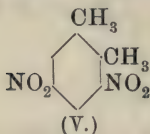
definitely established (compare this vol., p. 989). There would therefore appear to be only two possibilities (II and III) for the

constitution of this bromoxylenol, if it is accepted that, during the rearrangement, the ketonic group of the hydroaromatic substance becomes phenolic, and one of the methyl groups wanders into position 2:



Of these two formulæ the latter appears to be the more probable, because it has already been shown (compare this vol., p. 1297) that by the action of heat on dibromodimethylcyclohexenone (I), 6-bromo-*o*-4-xylenol (IV) is formed; that is to say, it is the bromine atom in position 5 of dibromodimethylcyclohexenone which remains in the resulting bromoxylenol, and this is therefore in all probability the bromine atom which would be found in the bromoxylenol in question. The production of the two xylenols would arise from the wandering in the one case of a methyl group from position 1 to position 2, and in the second case of a methyl group from position 1 to position 6; otherwise the rearrangement would be of an entirely similar nature.

In order to synthesise 5-bromo-*o*-3-xylenol, 3:5(4:6)-dinitro-*o*-



xylene (V) (T., 1909, **95**, 209) was converted into 5-nitro-*o*-3-xylidine (VI), as already described (T., 1911, **99**, 2351). In this substance the amino-group was replaced by hydroxyl, the resulting nitroxylene (VII) reduced to 5-amino-*o*-3-xylenol (VIII), in which compound the amino-group was replaced by a bromine atom, giving rise to 5-bromo-*o*-3-xylenol (IX), which was found to melt at 84°, and to be identical with the substance obtained by the action of phosphorus pentabromide on dimethyldihydroresorcin.

EXPERIMENTAL.

5-Nitro-*o*-3-xylidine (T., 1911, **99**, 2351), in quantities of 5 grams at one time, was suspended in 70 c.c. of 40 per cent. sulphuric acid

and diazotised by the addition of the requisite amount of a 20 per cent. sodium nitrite solution, at first at the temperature of the laboratory and afterwards at 50—60°. The whole was then poured into 120 c.c. of 40 per cent. sulphuric acid and heated on a water-bath until gas was no longer evolved. On cooling the oily mass, which at first separated, solidified. It was extracted with ether, the ethereal solution washed with sodium hydroxide, the washings acidified and allowed to stand, when the solid which separated was purified by crystallisation from chloroform and then benzene:

0.2120 gave 15.8 c.c. N_2 (moist) at 19° and 755 mm. $N=8.51$.

$C_8H_9O_3N$ requires $N=8.38$ per cent.

5-Nitro-*o*-3-xylenol, of which the yield of purified material is about 65—70 per cent. of the theoretical, is insoluble in light petroleum (b. p. 40—60°), very soluble in the acid in alcohol, acetone, or ethyl acetate, and crystallises from either chloroform or benzene in radiating clusters of small, orange-yellow needles, melting at 109°.

5-Nitro-*o*-3-xylenol was reduced in quantities of 2 grams at one time by dissolving in 100 c.c. of absolute alcohol, heating on the water-bath, and adding a saturated solution of sodium hyposulphite (Grandmougin, *Ber.*, 1906, **39**, 2494). After the addition of water, the solution was made alkaline with ammonium hydroxide and the alcohol evaporated. It is essential to get rid of the last traces of alcohol, as otherwise the yield of material is very considerably diminished. The resulting solid was crystallised from benzene, and analysed:

0.1303 gave 12.0 c.c. N_2 (moist) at 20° and 760 mm. $N=10.53$.

$C_8H_{11}ON$ requires $N=10.22$ per cent.

5-Amino-*o*-3-xylenol is readily soluble in the cold in acetone, or ethyl acetate, readily soluble in alcohol or water on warming, and crystallises from chloroform or benzene, in which solvents it is not easily soluble, in aggregates of small, orange needles, melting at 179°. The yield is about 40 per cent. of the theoretical.

Two grams of 5-amino-*o*-3-xylenol dissolved in 20 c.c. of water and 6 grams of 40 per cent. hydrobromic acid were diazotised at 0° with the calculated quantity of a 20 per cent. solution of sodium nitrite, the whole poured into a solution of 1 gram of cuprous bromide in 5 c.c. of 40 per cent. hydrobromic acid, allowed to stand for one hour, and then steam distilled. The solid, which passed over with the steam, was purified by crystallisation from light petroleum (b. p. 40—60°) and the bromine determined:

0.1104 gave 0.1031 AgBr. $Br=39.73$.

C_8H_9OBr requires $Br=39.80$ per cent.

5-Bromo-o-3-xyleneol is readily soluble in potassium hydroxide solution, alcohol, benzene, acetone, or chloroform, is insoluble in sodium carbonate solution, and crystallises from light petroleum (b. p. 40—60°) in radiating clusters of long, white, glistening needles, melting at 84°. The yield is only about 45—50 per cent. of the calculated on the aminoxyleneol used, and undoubtedly the easiest method for the preparation of this bromoxyleneol in large quantities is from hydroaromatic substances as will be described in a later communication.

The *benzoyl* derivative, prepared in the usual manner, is readily soluble in the cold in acetone, ethyl acetate, benzene, or chloroform, and crystallises from alcohol in colourless, transparent, rhombic plates, melting at 98°:

0.1188 gave 0.0743 AgBr. Br=26.61.

$C_{15}H_{13}O_2Br$ requires Br=26.23 per cent.

The *o-nitrobenzoyl* derivative, obtained in the ordinary way, is soluble in the cold in chloroform, ethyl acetate, acetone, or benzene, and crystallises from alcohol in radiating clusters of thin, glistening, transparent needles, melting at 128°:

0.2982 gave 10.6 c.c. N_2 (moist) at 20° and 759 mm. N=4.06.

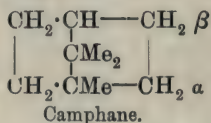
$C_{15}H_{12}O_4NBr$ requires N=4.00 per cent.

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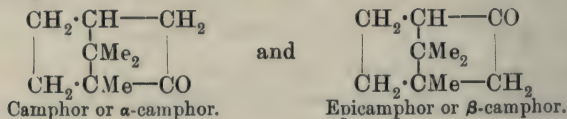
CCXXXI.—l-Epicamphor (l- β -Camphor).

By JULIUS BREDT and WILLIAM HENRY PERKIN, jun.

THE hydrocarbon from which camphor and its many derivatives may be said to be directly derived is camphane (Aschan, *Ber.*,



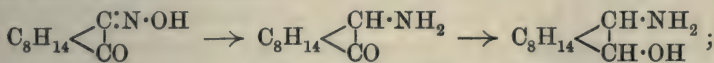
1900, **33**, 1009), and it is clear that this hydrocarbon must yield two different keto-derivatives by the substitution, on the one hand, of the α -, and on the other of the β - CH_2 group by CO, namely, the following:



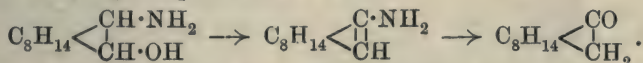
It is well known that Bredt (*Ber.*, 1893, **26**, 3047; *Annalen*, 1896, **292**, 33) originally suggested that the first of these formulæ most probably represents the constitution of camphor, and the correctness of this view has been abundantly proved by the great mass of experimental evidence which has accumulated, especially during the last few years.

The other possible isomeride—*epicamphor*—must be a substance the importance of which, at all events from the chemical point of view, can hardly be less than that of camphor itself, and indeed the study of the reactions and decompositions of epicamphor might be expected to afford clues to the constitution and relationship of some of the more complex derivatives of camphor which can hardly be obtained, or at least not so readily, from the study of camphor itself.

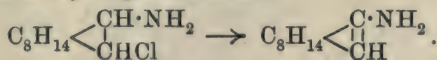
It is indeed obvious that the study of epicamphor, and especially the careful comparison of the properties of its derivatives with those of the corresponding derivatives of camphor, is a problem so attractive that it is not surprising to find evidence that repeated efforts have been made from time to time by different investigators to devise some process for the preparation of epicamphor, but, until recently, without success. In 1900, Duden and Macintyre (*Annalen*, **313**, 59) attempted to solve the problem by starting with *isonitrosocamphor*, which they first reduced to aminocamphor and then to aminoborneol:



they proposed then to remove water from the latter substance in order to obtain *l*-aminobornylene, from which, by the action of nitrous acid, *l*-epicamphor should result:



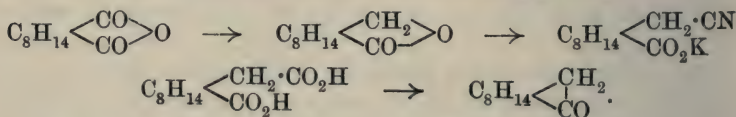
It was, however, not found possible to remove water directly from aminoborneol, and this base was therefore treated with phosphorus pentachloride, when it yielded α -chloro- β -aminocamphane, a substance which might be expected to yield aminobornylene by the elimination of hydrogen chloride:



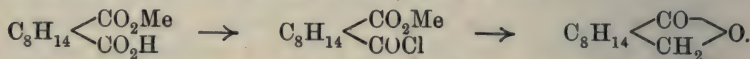
Elimination of hydrogen chloride did actually take place when the chloroamino-compound was distilled with aqueous sodium hydroxide, but the base (camphenamine) which was produced is not aminobornylene since, in place of epicamphor, it yields a substance having the properties of an unsaturated tertiary alcohol

(isocamphor) when it is treated with nitrous acid. It is therefore clear that intramolecular change must have taken place, probably during the elimination of hydrogen chloride from chloroaminophane.

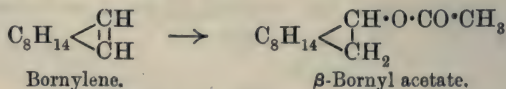
At a somewhat later date (*Compt. rend.*, 1905, **141**, 697) Haller and Blanc attempted to obtain epicamphor by a process similar to that which they had employed with success in the case of camphor itself. When camphoric anhydride is reduced by sodium amalgam it yields α -campholide, and this reacts with potassium cyanide to form an additive product, which, on hydrolysis, is converted into homocamphoric acid, and camphor is obtained by the distillation of the calcium or lead salt of this acid:



Haller and Blanc now prepared β -campholide from methyl hydrogen camphorate by conversion into the acid chloride and subsequent reduction with sodium and alcohol:



This substance should yield epicamphor by a process similar to that by which camphor had been obtained, but, unfortunately, all attempts to bring about combination between β -campholide and potassium cyanide were unsuccessful. An investigation which is of special importance in connexion with the present communication was published by Wagner in 1903 (*Chem. Zeit.*, **27**, 271; compare *Ber.*, 1903, **36**, 4602), since he there describes the preparation and derivatives of a substance which he claims to be epicamphor (β -camphor). Wagner subjected bornylene to the action of acetic acid and sulphuric acid, and thus converted it, by the well known Bertram and Walbaum process (*J. pr. Chem.*, 1894, [ii], **49**, 1), into a substance which he considered was the acetyl derivative of β -borneol:



This substance distilled at 229—230°/755 mm., and gave, on hydrolysis, the corresponding borneol (m. p. 203—204°), and, by oxidising this with permanganate, a ketone was obtained which distilled at 207—208°, melted at 160—161°, and this Wagner assumed to be β -camphor. He also prepared the oxime (m. p. 119—119.5°) and the semicarbazone (m. p. 201—202°).

The investigation of *l*-epicamphor, described in the present communication, shows, however, that the properties of this substance are in reality quite different from those of the substance obtained by Wagner.

l-Epicamphor melts at $183.5\text{--}184^\circ$, distils at 212° , yields an oxime melting at $103\text{--}104^\circ$ and a semicarbazone melting at $236\text{--}238^\circ$, and *l*-epiborneol melts at 182° .

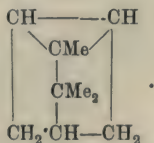
On the other hand, camphor melts at 179° , distils at 207° , yields an oxime melting at 119° and a semicarbazone melting at $246\text{--}248^\circ$, and borneol melts at 203° .

The researches of Brecht (*Annalen*, 1909, **366**, 52) have shown conclusively that the hydrocarbon employed by Wagner in his experiments could not have been pure bornylene, but must have been a mixture of bornylene and camphene or cyclene.*

There can therefore be little doubt that the ketone obtained by Wagner consisted largely of impure camphor, and this view is borne out by some of the physical properties which he ascribed to his product and its derivatives. In order to obtain further evidence on this point, Brecht and Hilbing (*J. pr. Chem.*, 1911, [ii], **84**, 783) investigated the addition of acetic acid to pure bornylene, and obtained a large yield (86 per cent.) of an ester distilling at $103\text{--}104^\circ/14\text{ mm.}$, but this was not a single substance, since it yielded on hydrolysis a mixture of borneols melting at $175\text{--}178^\circ$, which could not be separated by fractional crystallisation, and the only substance that could be obtained by the oxidation of this mixture was camphor.

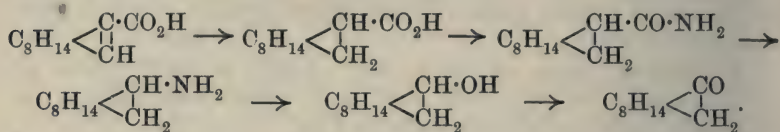
Before proceeding to a description of the methods by which *l*-epicamphor may now be obtained, some of the processes which were tried without success may be briefly mentioned. In the first place, *d*-bornylene-3-carboxylic acid was reduced to camphan-3-carboxylic acid (p. 2198); the amide of this was prepared, and submitted to the Hofmann reaction with the object of obtaining β -bornylamine, from which, by the action of nitrous acid, β -borneol

* Tschugaev (*Annalen*, 1912, **388**, 280) considers that the by-product obtained during the preparation of bornylene by the decomposition of methyl bornyl xanthate, $\text{C}_{10}\text{H}_{17}\text{O}\cdot\text{CS}_2\text{Me}$, consists of cyclene,

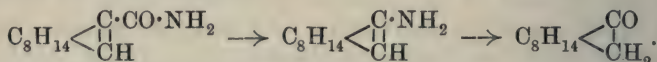


It is remarkable that this hydrocarbon, which is so stable to permanganate that it may be purified by oxidising the mixture with bornylene with permanganate until the latter hydrocarbon is destroyed (compare Henderson and Caw, *T.*, 1912, **101**, 1416), should be oxidised by hydrogen peroxide more readily than bornylene.

(epiborneol) should result, and be converted, by oxidation, into epicamphor:

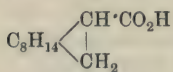


Experiment showed that a basic substance is actually obtained in this way, and this reacted with nitrous acid, but the product proved to be a mixture of borneols, and attempts to separate these have, so far, been unsuccessful. *d*-Bornylene-3-carboxylic acid itself was next converted into the amide in the hope that, by the careful application of the Hofmann reaction, this might yield the β -amino-bornylene which Duden and Macintyre (*loc. cit.*) had endeavoured to prepare, since this substance would doubtless react with nitrous acid to yield epicamphor:

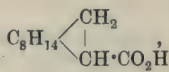


These various interactions resulted in the formation of a small quantity of a neutral substance, which was quite homogeneous, melted at 135°, and was evidently a ketone, since it reacted readily with phenylhydrazine. Examination showed, however, that it contained halogen, and it is probable that this substance was bromoepicamphor (p. 2210), which melts at the same temperature. Many other processes, which seemed likely to lead to the formation of epicamphor, were also investigated, but it is unnecessary to discuss these here. The first published account of the preparation of *l*-epicamphor is contained in a notice by F. R. Lankshear and W. H. Perkin, jun. (P., 1911, **27**, 167), in which it is shown that this substance may be obtained from *d*-camphane-3-carboxylic* acid by the following process. The chloride of this acid is treated with bromine, the product poured into alcohol, and the bromo-ester thus obtained digested with potassium acetate in acetic acid solution. After hydrolysis with alcoholic potassium hydroxide, the crude α -hydroxycamphane-3-carboxylic acid is oxidised by lead peroxide,

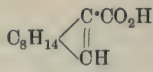
* In order that the letters α - and β - may be reserved in the usual manner for indicating the position of substituents in relation to the carboxyl group, the following scheme of nomenclature for the camphane- and bornylene- carboxylic acids has been adopted:



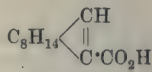
Camphane-
3-carboxylic acid.



Camphane-
2-carboxylic acid.

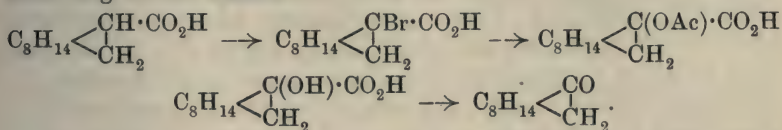


Bornylene-
3-carboxylic acid.

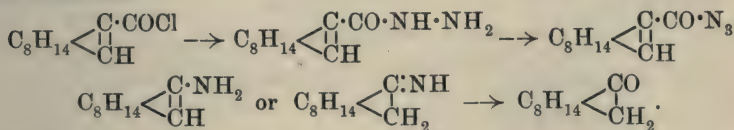


Bornylene-
2-carboxylic acid.

permanganate, or chromic acid, when *l*-epicamphor is obtained according to the scheme:



The first specimens of *l*-epicamphor, obtained in this way, were too small to allow of purification by means of the semicarbazone or by recrystallisation, and the melting point given (about 165°) was that of the crude product. Subsequently, considerable quantities (30 grams) were prepared by this process, and the purified substance then melted at 178—182°, had $\alpha_D -57.9$, and yielded an oxime melting at 103° and a semicarbazone melting at 236°. While these researches were in progress, Bredt and his co-workers had also succeeded in preparing *l*-epicamphor by a different method, and a preliminary account of this investigation appeared in the same year (*Chem. Zeit.*, 1911, **35**, 765). The process which these investigators employed was the conversion of *d*-bornylene-3-carboxylic acid, through the acid chloride, into the hydrazide, which, when subjected to the Curtius method, yielded the azide, and from this, by boiling with hydrochloric acid, *l*-epicamphor was obtained:

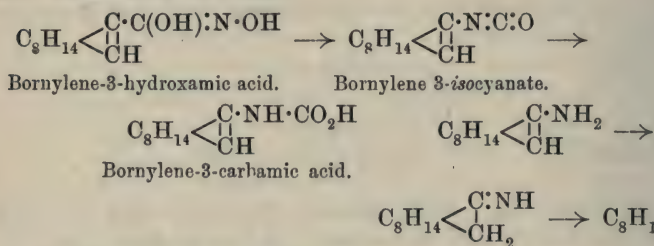


Since epicamphor had been obtained simultaneously in the laboratories at Aachen and Manchester, it was thought that the best plan would be to join forces; this was done, and the present publication is the result of that arrangement. Of the two processes just indicated for the preparation of *l*-epicamphor, the azide method is much to be preferred, because it not only gives much better yields, but also a purer product. It has this serious drawback, however, that there is always danger of explosion during the formation and extraction of the azide, and the process can therefore only be carried out safely with comparatively small quantities of material. For these reasons a large number of experiments were made with the object of devising a more satisfactory process for the preparation of epicamphor than either of those mentioned above, and, after many failures, this was ultimately accomplished with the aid of *d*-bornylene-3-hydroxamic acid.

This acid is produced almost quantitatively when methyl

d-bornylene-3-carboxylate is treated with hydroxylamine in the presence of sodium methoxide (compare Lossen, *Annalen*, 1875, **175**, 313; **178**, 213; Thiele and Pickard, *Annalen*, 1899, **309**, 189); it is a crystalline substance, and is remarkable for the ease with which it is converted into *l*-epicamphor under a variety of conditions. When a small quantity of the acid is heated alone, it decomposes just above its melting point (136°), with almost explosive violence and development of much heat; ammonia, and steam are liberated, and epicamphor is formed. The principal product of the decomposition is, however, a pale yellow, transparent resin, which may be distilled, and this, in contact with hydrochloric acid and subsequent distillation in steam, gives a large yield of epicamphor.

The explanation of this curious decomposition is probably the following: Bornylene-3-hydroxamic acid on heating loses water, the product undergoes molecular rearrangement, and the yellow, volatile resin is bornylene 3-*isocyanate*. The water produced during this process decomposes some of the *isocyanate*, with formation of epicamphor and ammonia, and the remainder is decomposed in the same direction by the subsequent treatment with hydrochloric acid and distillation in steam:



The sodium salt of *d*-bornylenehydroxamic acid also decomposes with considerable violence at as low a temperature as 105°, and the product, on treatment with hydrochloric acid, yields *l*-epicamphor, and, again, the aqueous solution of the sodium salt gradually clouds when it is boiled, owing to the separation of epicamphor. These pyrogenetic decompositions, owing to their violence, are not suitable as methods of preparation of epicamphor, but the discovery that the acetyl and benzoyl derivatives of *d*-bornylenehydroxamic acid, which decompose in a similar manner, do so more quietly, led ultimately to the working out of a valuable method for the preparation of epicamphor, which consists in bringing about the intramolecular change mentioned above, with the aid of toluene-*p*-sulphonyl chloride and several hundred grams of *l*-epicamphor have been made in this way (compare p. 2206).

This method of preparation gives a good yield of *l*-epicamphor,

and its great advantage over the azide process (p. 2187) lies in the fact that it proceeds without the risk of explosion, and may therefore be carried out with comparatively large quantities of material.

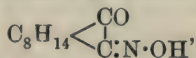
All the methods for obtaining *l*-epicamphor which are at present available have *d*-bornylene-3-carboxylic acid for their starting point, and not only is the preparation of this acid a long and tedious process, but its subsequent conversion into epicamphor involves a complicated series of reactions, and thus, with ordinary laboratory apparatus, several months are required in order to prepare two or three hundred grams of epicamphor.

It is therefore to be hoped that the further experiments on which we are at present engaged will lead to the discovery of a simpler method for the preparation of this important substance.

Comparison of the Properties of l-Epicamphor with those of d-Camphor.

l-Epicamphor has an odour very similar to, but yet distinct from, that of camphor, it melts at 182° , distils at 213° , and is lævorotatory, the value for α_D in benzene being -58.21° ; epicamphoroxime melts at $103\text{--}104^{\circ}$, and has $\alpha_D + 100.5^{\circ}$; epicamphorsemicarbazone melts at $237\text{--}238^{\circ}$; on oxidation, epicamphor yields *d*-camphoric acid.

d-Camphor melts at $177\text{--}178^{\circ}$, distils at 207° , and has $\alpha_D + 39.1^{\circ}$ in benzene; the oxime melts at 119° , and has $\alpha_D - 56.0^{\circ}$, and the semicarbazone melts at $247\text{--}248^{\circ}$.* When *l*-epicamphor is treated, in ethereal solution, with *iso*amyl nitrite and sodamide, it yields the two stereoisomeric isonitroso-*l*-epicamphors,



the α -modification melts at $168\text{--}170^{\circ}$ and has $\alpha_D - 201.9^{\circ}$, and the β -modification melts at $138\text{--}140^{\circ}$, and has $\alpha_D - 183.5^{\circ}$, and of these the latter is the unstable form, since it is converted into the former by melting or boiling with water. These two isonitroso-*l*-epicamphors have also recently been prepared by Forster and Spinner by another process (T., 1912, 101, 1348), and correspond with the two isonitrosocamphors, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C:N}\cdot\text{OH} \\ \diagdown \\ \text{CO} \end{array}$, which melt at $152\text{--}153^{\circ}$ and 114° , and have respectively $\alpha_D + 196.6^{\circ}$ and

* The semicarbazone of camphor was first prepared by Tiemann (*Ber.*, 1895, 28, 2191), who stated that it melts at $236\text{--}238^{\circ}$, and this is usually given as the actual melting point. Rimini (*Gazzetta*, 1900, 30, 603) pointed out, however, that the true melting or decomposing point is 245° , and we have prepared this substance in different ways and also find that it melts and decomposes at 245° or $247\text{--}248^{\circ}$ (corr.)

+172.9°, and in this case also the higher melting isomeride is the stable form, since it is readily formed from the isomeride of lower melting point by the action of heat. The α - and β -modifications of *isonitroso-l-epicamphor* both yield camphorquinone on treatment with formaldehyde and hydrochloric acid, and are converted into the imide of *d-camphoric acid* by heating with sulphuric acid, and these are reactions which are also shown by the *isonitroso-camphors*.

Reduction with zinc dust and sodium hydroxide converts both α - and β -*isonitroso-l-epicamphor* into the same *amino-l-epicamphor*,

$C_8H_{14} \begin{smallmatrix} \text{CO} \\ \diagup \\ \text{CH} \cdot \text{NH}_2 \end{smallmatrix}$, which melts at 168—170°, has, in benzene, $\alpha_D + 15^\circ$, and is a substance which crystallises well, and is comparatively stable, whereas aminocamphor, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NH}_2 \\ \diagup \\ \text{CO} \end{smallmatrix}$, melts

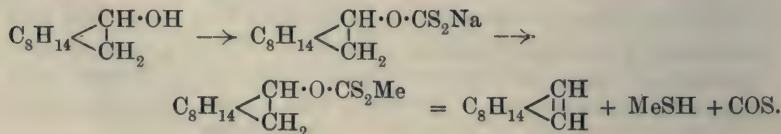
at 226—228°, and is a waxy substance, which readily undergoes change (compare Duden and Pritzkow, *Annalen*, 1899, **307**, 209).

l-Epicamphor is readily reduced when sodium is dissolved in its boiling alcoholic solution, with the formation of *l-epiborneol*,

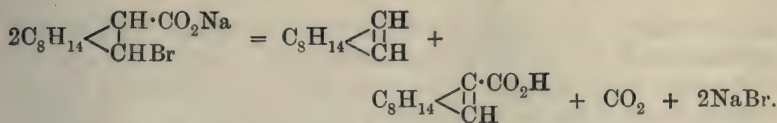
$C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{OH} \\ \diagup \\ \text{CH}_2 \end{smallmatrix}$, a crystalline substance, which melts at 181—182.5°,

and yields a phenylurethane melting at 82°. It is remarkable that epiborneol has no rotation, but it is not really an inactive substance, as is shown by the fact that, when it is converted by loss of water into the hydrocarbon, the substance which results is *l-bornylene*, with the rotation $\alpha_D - 18.45^\circ$.

For the purpose of the elimination of water, *l-epiborneol* was converted, by the action of sodium and then of carbon disulphide, into *l-epibornyl xanthate*, and then, by treatment with methyl iodide, into methyl *l-epibornyl xanthate*, which, on distillation, is decomposed with elimination of methyl mercaptan and carbonyl sulphide, and formation of *l-bornylene* (method of Tschugaev):



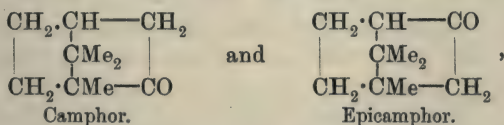
The *l-bornylene*, produced in this way, melted at 114°, and had, in solution in toluene, $\alpha_D - 18.45^\circ$; it yielded *d-camphoric acid* on oxidation, and was evidently identical with the *l-bornylene* which Bredt (*Annalen*, 1909, **366**, 46) had previously obtained by the decomposition of sodium β -bromodihydrobornylenecarboxylate by boiling with water:



During the experiments on the reduction of *l*-epicamphor with sodium and alcohol we have endeavoured to determine whether, besides *l*-epiborneol, a second isomeride (*epiisoborneol*) is produced, and, although the melting points of different specimens varied slightly and seemed to indicate that such a substance might be present, if this is the case, it must be present in small quantity, and we have not been able to isolate it. Bertram and Wahlbaum (*J. pr. Chem.*, 1894, [ii], **49**, 12; compare Wallach, *Annalen*, 1885, **230**, 225) have shown that the product of the reduction of *d*-camphor with sodium and alcohol contains, besides *d*-borneol, sometimes as much as 20 per cent. of *l*-isoborneol.

d-Borneol melts at 208°, has $\alpha_D + 38.39^\circ$, and, like *l*-epiborneol, yields *l*-bornylene when it is converted into the methyl xanthate, and this is distilled. *l*-isoBorneol, obtained from *d*-camphor by reduction, melts at 212°, and has $\alpha_D - 33^\circ$.

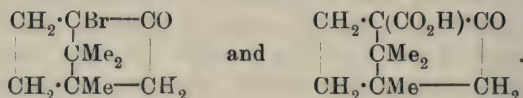
If the formulæ of camphor and epicamphor are compared it is



at once evident that, apart from the relative positions of the carbonyl and methylene groups, the most striking difference is that one of the linkings of the carbonyl group is attached to the tertiary $>\text{CMe}$ group in the case of camphor, whereas, in epicamphor, it is attached to the secondary $>\text{CH}$ group, and it was therefore to be expected that the carbonyl group of epicamphor might show greater reactivity than that in camphor. It is well known that camphor does not combine with hydrogen cyanide, but we were surprised to find that, in spite of the presence of the $>\text{CH} \cdot \text{CO} \cdot \text{CH}_2$ -group in epicamphor, this substance is also not capable of yielding an additive product with hydrogen cyanide, at all events, under the favourable conditions described on p. 2210. This is the more remarkable since Lapworth and Chapman (*T.*, 1901, **79**, 378) have shown that the $>\text{CO}$ group in camphorquinone combines quite readily with hydrogen cyanide; again, Manasse (*Ber.*, 1897, **30**, 662) has shown that camphorquinone may be reduced by zinc dust and acetic acid, whereas epicamphor is unchanged under the same conditions, and these results seem to indicate that any difference

in the relative reactivity of the carbonyl groups in camphor and epicamphor is, at the most, only a slight one.

Another consideration connected with the difference in the constitutional formulæ of camphor and epicamphor is the possibility that the presence of the $>\text{CH}$ group adjacent to the carbonyl group in epicamphor and its absence in camphor might well lead to a difference in the constitution of the substitution derivatives, and that, for example, whilst bromocamphor and camphorcarboxylic acid contain the groupings $-\text{CHBr}\cdot\text{CO}-$ and $-\text{CH}(\text{CO}_2\text{H})\cdot\text{CO}-$, the corresponding derivatives of epicamphor might have the following constitutions:



The sodium salt of *l*-epicamphorcarboxylic acid is produced when a boiling ethereal solution of *l*-epicamphor is treated with carbon dioxide in the presence of sodium, but it is more readily obtained and in much better yield when the solution of epicamphor in benzene is boiled with sodamide and a stream of carbon dioxide passed (p. 2214). The free acid melts at $120\text{--}122^\circ$, and is very similar in properties to *d*-camphorcarboxylic acid (m. p. $125\text{--}126^\circ$), since both acids are decomposed somewhat above their melting points into carbon dioxide and epicamphor or camphor respectively. Epicamphorcarboxylic acid gives a green coloration when ferric chloride is added to its alcoholic solution (camphorcarboxylic acid gives a blue in similar circumstances), and it therefore is clear that it must contain the grouping $>\text{CH}\cdot\text{CO}_2\text{H}$, and its formula must be $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CO} \\ | \\ \text{CH}\cdot\text{CO}_2\text{H} \end{smallmatrix}$, and not that suggested

above as a possible alternative. When this acid is treated with bromine at the ordinary temperature it yields bromo-*l*-epicamphorcarboxylic acid (m. p. 145°) and, as this acid gives no coloration with ferric chloride, its constitution must be that represented by the formula $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CO} \\ | \\ \text{CBr}\cdot\text{CO}_2\text{H} \end{smallmatrix}$.

Now this acid is decomposed when it is heated a few degrees above its melting point with elimination of carbon dioxide and formation of a bromo-*l*-epicamphor, which melts at 136° , has $\alpha_D - 86.6^\circ$ (bromocamphor melts at 76° and has $\alpha_D + 140^\circ$), and the constitution of this substance must evidently be $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CO} \\ | \\ \text{CH}\cdot\text{Br} \end{smallmatrix}$, a view which is confirmed by the fact that it yields *d*-camphoric acid when it is oxidised by dilute nitric acid. This same bromo-

epicamphor, however, is also obtained by the direct bromination of epicamphor (p. 2210), and it follows, therefore, that hydrogen of the $>\text{CH}_2$ group, and not of the $>\text{CH}$ group, is substituted during the conversion of epicamphor into epicamphorcarboxylic acid and bromoepicamphor.

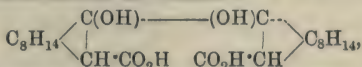
The l-Epiborneolcarboxylic Acids, l-Bornylene-2-carboxylic Acid, l-Camphane-2-carboxylic Acid, and the Conversion of l-Epicamphor into d-Camphor.

Roser, in 1885 (*Ber.*, **18**, 3114), first called attention to the fact that camphorcarboxylic acid, although it is a β -ketonic acid, cannot be reduced by sodium amalgam, and showed that reduction does not even take place under the conditions which so readily convert camphor into borneol, namely, when the acid or its ester is treated with sodium and alcohol. These observations were confirmed by Bredt (*Annalen*, 1906, **348**, 200; 1909, **366**, 1), who discovered, however, that camphorcarboxylic acid may be reduced electrolytically, using potassium amalgam as the cathode, and that it then yields two acids, namely, *cis*-borneolcarboxylic acid (m. p. 101–102°) and *cis-trans*-borneolcarboxylic acid (m. p. 171°), whereas four isomeric acids of the formula C_8H_{14} $\begin{matrix} \text{CH}\cdot\text{CO}_2\text{H} \\ | \\ \text{CH}\cdot\text{OH} \end{matrix}$ are theoretically possible.

Owing to the difference in constitution between epicamphorcarboxylic acid and camphorcarboxylic acid (compare p. 2192), it seemed possible that the former might exhibit less resistance to reducing agents than the latter, and experiment showed that epicamphorcarboxylic acid is actually reduced when the solution of its sodium salt is boiled with sodium amalgam, but the process is very slow and incomplete.

When, however, *l*-epicamphorcarboxylic acid was reduced electrolytically under the same conditions as camphorcarboxylic acid, it was more readily reduced than the latter, and yielded a product from which, by fractional crystallisation from light petroleum, four *l*-epiborneolcarboxylic acids, C_8H_{14} $\begin{matrix} \text{CH}\cdot\text{OH} \\ | \\ \text{CH}\cdot\text{CO}_2\text{H} \end{matrix}$, were separated, namely, A (m. p. 125°, $\alpha_D + 2.36^\circ$), B (m. p. 143–145°, $\alpha_D - 4.8^\circ$), C (m. p. 173°, $\alpha_D + 15.18^\circ$), and D (m. p. 237°, $\alpha_D + 77.9^\circ$)*. When a mixture of these acids is dehydrated with

* The results of analysis indicate that this isomeride of high melting point (D) may possibly be a pinacone acid of the formula

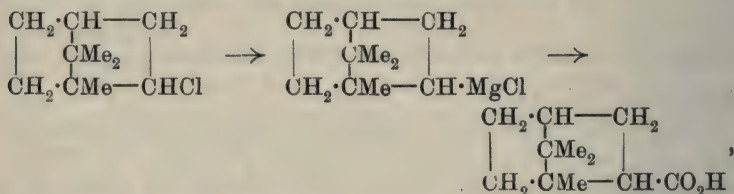


but this seems improbable in view of the fact that it dissolves almost as readily in

acetyl chloride and the product distilled, 1-bornylene-2-carboxylic acid, $C_8H_{14} \begin{smallmatrix} \text{CH} \\ | \\ \text{C} \cdot \text{CO}_2\text{H} \end{smallmatrix}$, is obtained, which melts at 115° , has $\alpha_D - 95.7^\circ$, and is very similar to *d*-bornylene-3-carboxylic acid, $C_8H_{14} \begin{smallmatrix} \text{C} \cdot \text{CO}_2\text{H} \\ | \\ \text{CH} \end{smallmatrix}$, (m. p. 112° , $\alpha_D + 149.5^\circ$), in its properties.

1-Camphane-2-carboxylic acid, $C_8H_{14} \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH} \cdot \text{CO}_2\text{H} \end{smallmatrix}$, is obtained in quantitative yield when *l*-bornylene-2-carboxylic acid is reduced by hydrogen in the presence of palladium and gum arabic (compare p. 2219); it melts at $78-80^\circ$, has $\alpha_D - 37.8^\circ$, and closely resembles *d*-camphane-3-carboxylic acid, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H} \\ | \\ \text{CH}_2 \end{smallmatrix}$, which melts at $90-91^\circ$, and is produced by the reduction of *d*-bornylene-3-carboxylic acid under the same conditions (p. 2198).

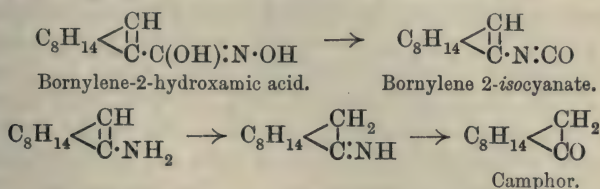
Epicamphane-2-carboxylic acid had already been prepared by Houben and Kesselkaul (*Ber.*, 1902, **35**, 3696) from pinene hydrochloride by conversion into the magnesium derivative and subsequent decomposition by carbon dioxide and water:



and these investigators state that the free acid crystallises and distils at $156^\circ/12$ mm. Zelinsky (*Ber.*, 1902, **35**, 4417; compare *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 646) prepared the same acid (called by him "camphanecarboxylic acid") from borneol by converting it into bornyl iodide, and then acting on this with magnesium and carbon dioxide, and he states that it melts at $69-71^\circ$. At a later date, Houben (*Ber.*, 1905, **38**, 3799) again prepared the acid (hydropinenecarboxylic acid) from pinene hydrochloride, and describes it as a crystalline substance, melting at $72-74^\circ$ and distilling at $153^\circ/13$ mm.

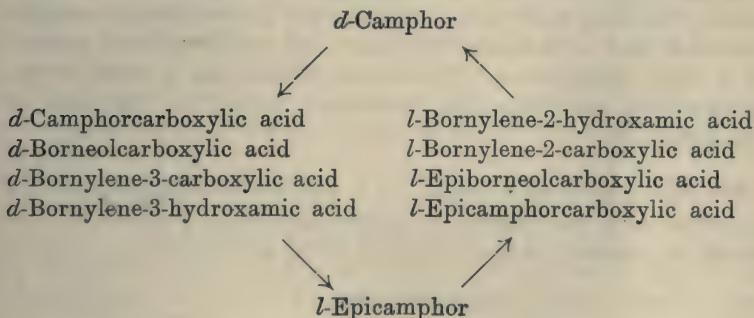
Methyl *l*-bornylene-2-carboxylate reacts readily with hydroxylamine in the presence of sodium methoxide, with the formation of 1-bornylene-2-hydroxamic acid, a syrup which, on heating, decomposes vigorously, and yields steam, ammonia, some camphor, and a pale yellow, resinous substance. The latter, which doubtless consists of bornylene 2-isocyanate, gives a large yield of *d*-camphor solvents as the other isomerides. and that an acid of this kind has not been observed among the products of the reduction of camphorcarboxylic acid.

when it is mixed with hydrochloric acid and distilled in steam, and the whole process, which may be represented thus:



is exactly similar to the formation of *l*-epicamphor from *d*-bornylene-3-hydroxamic acid under the same conditions. Lastly, the above intramolecular change was brought about by treating the sodium salt of *l*-bornylene-2-hydroxamic acid with toluene-*p*-sulphonyl chloride (compare p. 2221), and, after decomposing with hydrochloric acid, the product was distilled in steam, when a comparatively large yield of *d*-camphor was obtained. The *d*-camphor resulting from these two experiments melted at 176°, had, in ethyl acetate solution, $\alpha_D + 47.7^\circ$, and yielded an oxime melting at 119°, whereas ordinary *d*-camphor melts at 178°, has $\alpha_D + 48.0^\circ$, and camphoroxime melts at 119°.

The conversion of *l*-bornylene-2-carboxylic acid into *d*-camphor completes the interesting cycle, *d*-camphor \rightleftharpoons *l*-epicamphor, and the whole scheme may be clearly represented thus:



Comparison of some Physiological Properties of d-Camphor and l-Epicamphor.

The following experiments, which deal with the comparative action of camphor and epicamphor on the beat of the heart in a frog, following the administration of chloral, were carried out by Professor van der Velden and Dr. P. Leyden in the laboratories of the Mediz. Klinik der Akademie für prakt. Mediz. in Düsseldorf.

The administration of a drop of a 5 per cent. oil solution of

camphor doubled the beat of the heart from thirteen to twenty-six, and the heart curve tracing was unusually regular; the same experiment with epicamphor showed no appreciable action. When a 10 per cent. oil solution of camphor was employed, it was found that three drops increased the beat from seven to twenty-two, and that the beat then became very constant, and the curve tracing was again remarkably regular. The same quantity of epicamphor increased the beat slowly from six to twelve, and then a gradual decrease was observed and the beat became very irregular.

The administration of three drops of a 20 per cent. oil solution of camphor increased the beat from six to eighteen; then a decrease to eleven occurred, and the well-known poisonous action of camphor became evident.

In a similar experiment with epicamphor the beat was increased from six to twenty-seven, but rapidly decreased to thirteen in five minutes. A subsequent administration had no further effect, and the curve, which at first was very regular, became weaker.

These results show that favourable action of epicamphor on the beat of the heart does not become apparent until the solution administered is about four times stronger than that which produces the same effect in the case of camphor. A further series of experiments has, moreover, clearly shown that, even at this concentration, epicamphor has not the same favourable action as camphor because the effect soon disappears, whereas in the case of camphor (provided that it is absolutely pure) the action induced persists for a much longer time. The action of camphor is toxic at the concentration necessary for favourable action in the case of epicamphor.

We are at present engaged in a further investigation of the properties and derivatives of epicamphor, and hope shortly to publish an account of the results of these experiments.

EXPERIMENTAL.*

d-Bornylene-3-carboxylic Acid and its Derivatives.

The preparation of bornylene-3-carboxylic acid from camphor-carboxylic acid by electrolytic reduction to the isomeric borneol-

* Wilhelm Hilbing and Joseph Regout assisted Prof. Bredt in Aachen, the former in the preparation of epicamphor by the bornylenecarboxylic acid azide method and in converting it into the oxime, semicarbazone, and into epicamphorcarboxylic acid by the sodium, carbon dioxide, process, and also in preparing several derivatives of bornylenecarboxylic acid, such as the ester, acid chloride and amide; the latter prepared most of the epiborneol employed in this research, and converted it into bornylene by the Tschugaev xanthate method.

Mr. F. R. Lankshear assisted Prof. Perkin by preparing much of the bornylene-

carboxylic acids and subsequent elimination of water, has already been described by Bredt and his co-workers (*Annalen*, 1906, **348**, 200; 1909, **366**, 1).

The acid employed in the present research was purified by distillation either alone or in a current of steam or by recrystallisation from acetone, from which it separates in large, colourless crystals; it melts at 112—113°, distils at 156—157°/13 mm., and yields an anhydride, which melts at 96—97° and distils at 236°/21 mm.

The *barium* salt, $(C_{10}H_{15}\cdot CO_2)_2Ba, 4H_2O$, was prepared by dissolving the acid in pure barium hydroxide, and, after removing the excess of the latter by carbon dioxide and concentrating the filtrate, the salt separated in needles. For analysis it was recrystallised from water, and then exposed to the air for several days:

0.2738, on drying at 120°, lost 0.0360 H_2O and gave 0.1112 $BaSO_4$. $H_2O=13.2$; $Ba=24.2$.

$(C_{11}H_{15}O_2)_2Ba, 4H_2O$ requires $H_2O=12.7$ and $Ba=24.2$ per cent.

The *acid chloride*, $C_{10}H_{15}\cdot COCl$, may be prepared by adding the acid (20 grams) to phosphorus pentachloride covered with light petroleum (100 c.c., b. p. 35—60°), and after the vigorous decomposition has subsided, the whole heated on the steam-bath for two hours, the light petroleum distilled off, and the residue fractionated under diminished pressure.

This chloride may be prepared even more conveniently by warming equal weights of the acid and thionyl chloride; as soon as the reaction is complete, the product is distilled, when an almost quantitative yield of the pure chloride is obtained.

Bornylene-3-carboxyl chloride distils at 120—121°/19 mm., and is a comparatively stable substance, which fumes only slightly in the air:

0.2600 gave 0.1811 $AgCl$. $Cl=17.3$.

$C_{11}H_{15}OCl$ requires $Cl=17.8$ per cent.

The *acid amide*, $C_{10}H_{15}\cdot CO\cdot NH_2$.—This substance may be prepared from the anhydride by heating with concentrated aqueous ammonia at 100°, when a clear solution is obtained, from which the amide crystallises on cooling. A specimen was also prepared by gradually adding the acid chloride to concentrated aqueous ammonia, the whole being well cooled and stirred during the

3-carboxylic acid used in Manchester for the preparation of epicamphor and by photographing the absorption spectra of epicamphor and its derivatives. Valuable assistance was also rendered by Messrs. Reginald Furness and Harold Goodwin, not only in the preparation of bornylenecarboxylic acid, but also in working out the details of the formation of epicamphor by the bornylenehydroxamic acid process, of the preparation of epicamphorcarboxylic acid by the sodamide—carbon dioxide method, and of the conversion of epicamphor into camphor.

operation. The amide is best crystallised from dilute ammonia, from which it at first frequently separates as a milky precipitate, but on rubbing or the addition of a crystal, crystallisation at once sets in. It melts at 119—122°, and yields a crystalline hydrochloride when its solution in light petroleum is saturated with hydrogen chloride, but this is unstable, and decomposes on keeping:

0.2367 gave 16 c.c. N_2 at 18° and 752 mm. $N=8.0$.

$C_{11}H_{17}ON$ requires $N=7.8$ per cent.

The *methyl* ester, $C_{10}H_{15} \cdot CO_2Me$.—The esters of bornylene-3-carboxylic acid must not be prepared by the action of the acid chloride on the alcohols or by saturating the alcoholic solutions of the acid with hydrogen chloride, because the esters obtained in both cases, although they distil constantly, invariably contain chlorine. The large quantities of the methyl ester used in this research were prepared as follows: The pure acid (10 grams), dissolved in methyl alcohol (50 grams) and sulphuric acid (5 grams), was left for twenty-four hours, and then heated on the steam-bath for two hours. After diluting with water, the ester was extracted with ether, washed with water and dilute sodium carbonate, dried, and distilled.

Under these conditions, esterification is practically complete, and the methyl ester distils at 158°/100 mm.:

0.1112 gave 0.3021 CO_2 and 0.0941 H_2O . $C=73.9$; $H=9.4$.

$C_{12}H_{18}O_2$ requires $C=74.2$; $H=9.4$ per cent.

1.6464, made up to 20 c.c. in ethyl acetate, gave $\alpha_D + 100.5^\circ$.

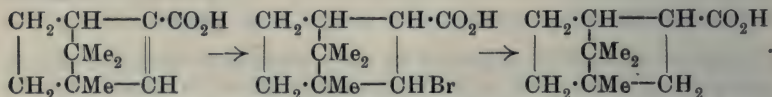
The *ethyl* ester, prepared in a similar manner, distils at 115°/12 mm. or 168°/100 mm.:

0.1211 gave 0.3330 CO_2 and 0.1079 H_2O . $C=74.9$; $H=9.9$.

$C_{13}H_{20}O_2$ requires $C=75.0$; $H=9.6$ per cent.

d-Camphane-3-carboxylic Acid.

Camphane-3-carboxylic acid was first prepared by Bretz (*Annalen*, 1909, **366**, 60) from *d*-bornylene-3-carboxylic acid by conversion into β -bromohydrobornylene-3-carboxylic acid (β -bromocamphane-3-carboxylic acid) and subsequent reduction by potassium amalgam:



A more direct and convenient process is the reduction of bornylenecarboxylic acid by hydrogen in the presence of palladium and gum arabic under the conditions recommended by Skita (*Ber.*, 1909, **42**, 1630).

Pure bornylene-3-carboxylic acid (10 grams) dissolved in methyl alcohol was mixed with 5 c.c. of a 20 per cent. gum arabic solution and 0.5 gram of palladium chloride; 150 c.c. of hot water was then added, and the whole placed in a long, narrow cylinder, and hydrogen passed for several hours. The product was rendered alkaline by sodium carbonate, the methyl alcohol and most of the water distilled off, the solution filtered, acidified, and the crude camphanecarboxylic acid, which separated as a crystalline mass, collected and distilled in steam. The acid, which was not quite stable to permanganate, was dissolved in sodium carbonate, mixed with powdered ice, and left in contact with excess of permanganate for half an hour; the permanganate was then destroyed by sulphur dioxide, and the filtrate from the manganese precipitate concentrated and acidified. Finally, the camphane-3-carboxylic acid was recrystallised from dilute acetic acid, from which it separated as a voluminous mass of thin plates, and melted at 90—92°:

0.1072 gave 0.2847 CO₂ and 0.0951 H₂O. C=72.4; H=9.9.

C₁₁H₁₈O₂ requires C=72.5; H=9.9 per cent.

Conversion of d-Camphane-3-carboxylic Acid into l-Epicamphor.

This process, which is discussed on p. 2186, may be carried out under the following conditions: *d*-Camphane-3-carboxylic acid (18 grams) is mixed with phosphorus pentachloride (22 grams) in a flask fitted with a ground-in air-tube, heated on the steam-bath until decomposition is complete, and, after cooling, bromine (18 grams) is added, and the whole transferred to a pressure-tube and gradually heated in a water-bath for several hours. The product, which is almost free from bromine, is poured into alcohol, and, after remaining for twenty-four hours, water is added and the bromo-ester extracted with ether.

The ethereal solution is thoroughly washed with water, carefully dried, evaporated, and the residue mixed in a reflux apparatus with glacial acetic acid (50 c.c.) and anhydrous potassium acetate (20 grams) and heated in the oil-bath to boiling for forty-five minutes, when potassium bromide separates in quantity and there is some darkening.

The product is diluted with water, extracted with ether, the ethereal solution washed well, evaporated, and left during twenty-four hours with a solution of potassium hydroxide (25 grams) in methyl alcohol.

After heating for three hours on the steam-bath, the methyl alcohol is removed by evaporation, the residue then acidified and extracted with ether, when, on evaporation, crude α -hydroxy-

camphane-3-carboxylic acid remains as a pale brown syrup, and *l*-epicamphor was obtained from this in three different ways:

I. *By Oxidation with Permanganate*.—The syrupy acid (5 grams) was dissolved in a slight excess of dilute potassium hydroxide, gradually mixed with permanganate (1.5 grams), and the whole heated on the steam-bath until oxidation was complete. After acidifying with sulphuric acid, the same quantity of permanganate was again added, and the whole distilled in a current of steam, when a semi-solid mass passed over, which consisted of a mixture of epicamphor and bornylene-3-carboxylic acid. The distillate was made alkaline with dilute potassium hydroxide, extracted with ether, the ethereal solution dried, and the ether removed by careful distillation with a column, when a buttery mass resulted (0.7 gram), which in contact with porous porcelain became quite dry and melted at 165° (compare Lankshear and Perkin, P., 1911, 27, 166), and, on treatment with hydroxylamine hydrochloride and sodium acetate, yielded *l*-epicamphoroxime melting at 102° (p. 2208).

Subsequently, a larger quantity of *l*-epicamphor (30 grams) was prepared by this process, and purified by conversion into the semicarbazone (p. 2209); it then melted at 178 – 182° , and yielded the following results on analysis:

0.1071 gave 0.3089 CO_2 and 0.1034 H_2O . C=78.7; H=10.7.

$\text{C}_{10}\text{H}_{16}\text{O}$ requires C=79.0; H=10.5 per cent.

II. *By Oxidation with Chromic Acid*.—In this experiment crude hydroxycamphanecarboxylic acid (3 grams), dissolved in a little water, was gradually mixed with an aqueous solution of chromic acid (1 gram), care being taken that the temperature did not rise above 35° .

When the product was heated in a steam distillation apparatus, carbon dioxide was eliminated, and an oil passed over which had the pungent odour of epicamphor, and on cooling became a butter-like mass.

This was collected and left in contact with porous porcelain until dry; it then melted at about 165 – 167° , and was proved to consist of epicamphor by conversion into the oxime (m. p. 102°) and the semicarbazone (m. p. 235 – 237°).

III. *By Oxidation with Lead Peroxide*.—In this experiment the crude hydroxycamphanecarboxylic acid (7 grams) was mixed with water (5 c.c.) and acetic acid (100 c.c.); precipitated lead peroxide (20 grams) was then added, and, after boiling for ten minutes in a reflux apparatus, during which carbon dioxide was evolved, the whole was distilled in steam, when epicamphor distilled as a buttery mass, and a further small quantity was obtained by adding more

lead peroxide and continuing the distillation. The distillate was extracted with ether, the ethereal solution shaken with sodium carbonate, which removed a considerable quantity of bornylene-3-carboxylic acid, dried, and evaporated, when crude epicamphor (2 grams) was obtained, which, in contact with porous porcelain, became quite hard, and was identified as before by conversion into the oxime (m. p. 103°) and semicarbazone (m. p. $235-237^{\circ}$).

Preparation of l-Epicamphor from d-Bornylene-3-carboxylic Acid by the Azide Method of Curtius.

It is remarkable that the bornylene-3-carboxylic hydrazide, $C_{10}H_{15} \cdot CO \cdot NH \cdot NH_2$, necessary for this process is a substance which is very difficult to obtain except under certain very definite conditions.

In the first experiments, bornylenecarboxylic ester was treated with hydrazine hydrate in the usual manner (Curtius, *J. pr. Chem.*, 1894, [ii], 50, 275) in or without the presence of alcohol, in the cold and at the boiling temperature, but in no case was the normal hydrazide obtained, and the only crystalline product which could be isolated was always the dibornylene-3-carboxylic hydrazide, $C_{10}H_{15} \cdot CO \cdot NH \cdot NH \cdot CO \cdot C_{10}H_{15}$, a description of which is given below. The action of the acid chloride on hydrazine hydrate was next investigated in the hope that the equation:

$C_{10}H_{15} \cdot COCl + 2N_2H_4 \cdot H_2O = C_{10}H_{15} \cdot CO \cdot NH \cdot NH_2 + N_2H_4 \cdot HCl + H_2O$ might be realised, but, except when the unusual conditions described below were employed, the result was always a negative one.

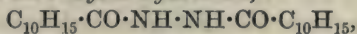
Thus, for example, when bornylenecarboxyl chloride was rubbed in a mortar with excess of hydrazine hydrate, a rather vigorous reaction set in with considerable development of heat, and this was checked by keeping the containing vessel in a freezing mixture. After an hour the product was mixed with water, the solid collected, washed with water and dilute sodium carbonate, and then crystallised from benzene or dilute alcohol, from which it separated as a glistening mass of needles, which became soft at 218° and melted at about 224° :

0.1326 gave 0.3623 CO_2 and 0.1083 H_2O . $C = 74.5$; $H = 9.0$.

0.1428 „ 10.4 c.c. N_2 at 17° and 745 mm. $N = 8.2$.

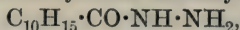
$C_{22}H_{32}O_2N_2$ requires $C = 74.2$; $H = 9.0$; $N = 7.8$ per cent.

Di-d-bornylene-3-carboxylic hydrazide,



is almost insoluble in water, but readily so in alcohol, and is a remarkably stable substance, since it is only very slowly decomposed when digested with alcoholic potassium hydroxide or hydrochloric acid.

Ultimately, normal *d*-bornylene-3-carboxylic hydrazide,



was obtained, in almost quantitative yield, by adding an alcoholic solution of hydrazine hydrate to an ethereal solution of the acid chloride under the following conditions: The pure acid chloride (20 grams), dissolved in dry ether (150 grams) and cooled to 0° , is gradually added from a jacketed funnel containing a freezing mixture to a solution of hydrazine hydrate (15 grams) in alcohol, which must be cooled below 0° . The liquid soon becomes milky, and needle-shaped crystals of hydrazine hydrochloride form on the sides of the vessel. After several hours, the clear solution is decanted from this salt and evaporated under diminished pressure, when a syrupy residue is obtained, which readily crystallises, and this mass is left for some days over concentrated sulphuric acid to remove the remainder of the alcohol. The white mass (19.5 grams) is almost pure, and may be recrystallised from benzene or a mixture of benzene and light petroleum, from which it separates in needles:

0.1944 gave 25.9 c.c. N_2 at 16.5° and 738 mm. $\text{N}=14.9$.

$\text{C}_{11}\text{H}_{18}\text{ON}_2$ requires $\text{N}=14.4$ per cent.

d-Bornylene-3-carboxylic hydrazide melts at $109\text{--}110^\circ$, and is readily soluble in alcohol, but sparingly so in ether or cold water; it dissolves readily in dilute hydrochloric acid, and is reprecipitated on the addition of sodium carbonate. The *hydrochloride*, which was required for the preparation of the azide, was obtained by dissolving the hydrazide (20 grams) in alcohol (25 grams) and adding a solution of alcoholic hydrogen chloride saturated at 0° (60 grams), when the hydrochloride separated at once. After remaining for two hours in ice-water, the crystalline precipitate was collected, washed with a little alcoholic hydrogen chloride, and left over solid potassium hydroxide in a vacuum desiccator for two days:

0.2210 gave 0.1380 AgCl . $\text{Cl}=15.4$.

$\text{C}_{11}\text{H}_{18}\text{ON}_2\cdot\text{HCl}$ requires $\text{Cl}=15.38$ per cent.

This hydrochloride melts and decomposes at 202° , and may be recrystallised either from water or alcohol, or best from a mixture of both. In a series of experiments the yields of the hydrazide and its hydrochloride from bornylenecarboxylic acid were the following:

One hundred grams of bornylenecarboxylic acid gave 103 grams of acid chloride (94 per cent.); this yielded 95 grams of hydrazide (94 per cent.), and from this, 103 grams of hydrochloride (92 per cent.) were obtained, or, the yield of hydrazide hydrochloride from 100 grams of bornylenecarboxylic acid is 80.6 per cent. of that theoretically possible.

Conversion of d-Bornylene-3-carboxylic Hydrazide into l-Epicamphor.

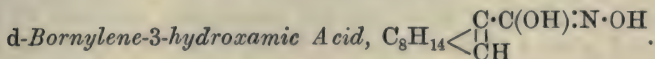
This experiment, which, owing to the well-known explosive nature of the azides, must be very carefully made and with small quantities of material, has been repeatedly carried out without accident under the following conditions: The hydrochloride of the hydrazide (10 grams) dissolved in water (200 c.c.) is covered with a layer of ether (100 c.c.), and the whole cooled in ice and salt. Sodium nitrite (3.1 grams) dissolved in a little water is then gradually added drop by drop, the temperature being maintained at 0° during the whole operation.

The addition of the nitrite produces a milkiness in the aqueous solution, but, by shaking, the oily azide passes into the ether, and at the end of the operation a few drops of dilute hydrochloric acid are added in order to ensure that nitrous acid is present in slight excess. The ethereal solution is separated, the aqueous layer extracted once with ether, and the combined extracts washed with ice-water, dried rapidly over calcium chloride, and mixed with alcohol (100 c.c.).

The ether is now removed on the steam-bath, and the alcoholic solution boiled in a reflux apparatus for two hours, and, after the alcohol has been distilled off under diminished pressure, a yellow syrup remains, which doubtless consists of the corresponding urethane.

This is dissolved in concentrated hydrochloric acid, and, after a few minutes, the solution is mixed with ice-water, when epicamphor separates in white flocks, and is best purified by distillation in steam, during which operation the bulk of the epicamphor, together with some bornylenecarboxylic acid, crystallises in the condenser. The whole is dissolved in ether, the bornylenecarboxylic acid carefully removed by repeated shaking with sodium carbonate, the ethereal solution dried, the ether slowly distilled off,* and the crude epicamphor left exposed to air with constant stirring until the residual ether has evaporated, and then placed in contact with porous porcelain, or the epicamphor may be directly distilled.

The yield of this nearly pure l-epicamphor is 5.5 grams.



After a long series of comparative experiments the best conditions for the preparation of this acid—a process which is also the

* Epicamphor is appreciably volatile with ether, and therefore the ether distilled from solutions of this substance was always carefully kept and used for subsequent extractions.

first step in the preparation of epicamphor (p. 2206)—appear to be the following.* Hydroxylamine hydrochloride (15 grams) is dissolved in hot methyl alcohol (100 c.c.), and, after cooling, mixed with a solution of sodium (4.6 grams) in methyl alcohol (60 c.c.). Methyl bornylene-3-carboxylate (39.2 grams) is then added, together with a solution of sodium (5 grams) in methyl alcohol (60 c.c.). After remaining over night in a cool place, during which crystals of the sodium salt of bornylene-3-hydroxamic acid (see below) frequently separate, the whole is heated in a thermostat at 50° for two days. The product (A) is rendered just acid by the addition of acetic acid, and mixed with excess of a concentrated solution of copper acetate, when a pale green, voluminous precipitate separates, which is collected, washed with water, drained on porous porcelain, and then dried at 60°. The powdered salt is covered with ether, saturated with hydrogen sulphide, at first in the cold and then at the boiling point; the filtrate and ether washings of the copper sulphide are evaporated, and the syrupy residue left over sulphuric acid in a vacuum desiccator until it crystallises, which it quickly does if it is rubbed from time to time. The nearly solid mass is left in contact with porous porcelain until free from oily impurity, and the colourless residue recrystallised from benzene, from which it separates as a voluminous mass of colourless, microscopic, hexagonal plates:

0.1243 gave 0.3077 CO₂ and 0.0954 H₂O. C=67.5; H=8.5.

0.1334 gave 8.5 c.c. N₂ at 16° and 761 mm. N=7.4.

C₁₁H₁₇O₂N requires C=67.7; H=8.7; N=7.2 per cent.

d-Bornylene-3-hydroxamic acid melts at 136°, and is readily soluble in alcohol, ether, or hot benzene, sparingly so in cold benzene, light petroleum, or cold water, but it dissolves readily in hot water. The aqueous solution gives, on the addition of ferric chloride, an intense claret coloration. The sodium salt, obtained as described above, crystallises from methyl alcohol, in which it is comparatively sparingly soluble in the cold, in glistening prisms, which become opaque on exposure to the air, and the air-dry substance loses approximately 14.6 per cent. over phosphoric oxide under diminished pressure. When the salt is heated in the water-oven, it gradually decomposes, and swells up into threads, and, if heated in a capillary tube, the salt decomposes suddenly at about 105° and gives a white sublimate, which melts to a syrup at about 110°. If the experiment is carried out in a test-tube with about 0.1 gram of the salt, and the product of the decomposition is

* This process is modelled on the preparation of phenylpropionylhydroxamic acid (hydrocinnamylhydroxamic acid), recommended by Thiele and Pickard (*Annalen*, 1899, 309, 197).

moistened with hydrochloric acid, diluted with water, and boiled, epicamphor distils with the steam, and crystallises on the cold part of the tube. Boiling with water also slowly decomposes the sodium salt, with the formation of epicamphor. When sulphuric acid is added to the dry salt an almost explosive decomposition occurs, and a white sublimate is formed. The sodium salt is very readily soluble in water, and yields, on the addition of hydrochloric acid, an immediate crystalline precipitate of the pure hydroxamic acid.

The Acetyl Derivative.—Bornylenehydroxamic acid dissolves gradually in twice its weight of pure acetic anhydride in the cold, and, after remaining for twenty-four hours, the product, on decomposition with water, yields a crystalline mass, which separates from benzene in hard prisms.

A still more convenient method of preparing this acetyl derivative is to moisten the sodium salt with acetic anhydride, and, after a few hours, to add water and purify the product by crystallisation from benzene:

0.1457 gave 0.3493 CO_2 and 0.1038 H_2O . $\text{C}=65.4$; $\text{H}=7.9$.

0.1569 „ 8.3 c.c. N_2 at 15° and 758 mm. $\text{N}=6.1$.

$\text{C}_{13}\text{H}_{19}\text{O}_3\text{N}$ requires $\text{C}=65.8$; $\text{H}=8.0$; $\text{N}=5.9$ per cent.

Acetylbornylene-3-hydroxamic acid melts at $115\text{--}116^\circ$, and is readily soluble in alcohol, ether, chloroform, or hot benzene, but it is comparatively sparingly soluble in cold benzene. It is very sparingly soluble in cold light petroleum, but separates well from the boiling solvent (b. p. $70\text{--}80^\circ$) in microscopic prisms. When the acetyl derivative is heated, it begins to decompose, with evolution of gas, at about 140° ; decomposition is rapid at 150° and at higher temperatures an oil distils which, when boiled with hydrochloric acid, yields epicamphor. When the solution of the sodium salt of bornylenehydroxamic acid was shaken with a slight excess of benzoyl chloride and a little sodium hydroxide, a thick gum was produced, which, after extraction with ether and thoroughly washing, crystallised. The substance separated from a mixture of benzene and light petroleum in colourless crusts, melted at about 123° , and was doubtless the *benzoyl* derivative of the hydroxamic acid:

0.1962 gave 8.4 c.c. N_2 at 18.6° and 761 mm. $\text{N}=4.9$.

$\text{C}_{18}\text{H}_{21}\text{O}_3\text{N}$ requires $\text{N}=4.7$ per cent.

On dry distillation this benzoyl derivative gives a pungent smelling oil, which when boiled with dilute hydrochloric acid develops the odour of epicamphor.

The Formation and Preparation of l-Epicamphor from d-Bornylene-3-hydroxamic Acid.

I. *Formation of l-Epicamphor by the Action of Heat on d-Bornylene-3-hydroxamic Acid.*—In studying this curious decomposition bornylenehydroxamic acid (5 grams) was gradually heated in a sulphuric acid bath until it just commenced to melt, when vigorous decomposition set in, a pale yellow resin was formed, and at the same time ammonia was eliminated, and a strong odour of epicamphor also became apparent. The product was shaken with hydrochloric acid, and, after remaining for fifteen minutes, water was added, when a brown syrup separated, which soon became semi-solid. The whole was now distilled in steam, which carried over epicamphor and left only a small, brown, resinous residue; the distillate was extracted with ether, the ethereal solution shaken with sodium carbonate,* dried, and evaporated, when 3 grams of crude epicamphor remained, and, after contact with porous porcelain and without further purification, had $\alpha_D -48.1^\circ$. For the purpose of complete identification, the substance was converted into the oxime (m. p. 103°) and semicarbazone (m. p. $236-238^\circ$).

II. *Preparation of l-Epicamphor from d-Bornylene-3-hydroxamic Acid by the Agency of Toluene-p-sulphonyl Chloride.*—This process, which has been employed for the preparation of more than 400 grams of epicamphor, is, in its first stage, carried out much in the way already described in the case of the preparation of bornylene-3-hydroxamic acid (p. 2204), except that epicamphor appears to be produced in larger yield when a considerable excess of hydroxylamine and sodium methoxide is used. Hydroxylamine hydrochloride (21 grams), dissolved in methyl alcohol (150 c.c.), is mixed with methyl bornylene-3-carboxylate (40 grams), sodium (14 grams), dissolved in methyl alcohol (180 c.c.), is then gradually added, the temperature being kept below 20° during this operation. After remaining for twenty-four hours, the product is heated in a thermostat at 50° for two days, cooled, mixed with powdered ice, and then toluene-p-sulphonyl chloride (65 grams) added, and the whole vigorously shaken in a bottle on the machine for twelve hours continuously.

It is most important that the decomposition of the sodium salt of the hydroxamic acid by the sulphonyl chloride should be as complete as possible, and the shaking must therefore be very thorough, and as some heat is developed during the first two hours, care is taken to cool the bottle and release the pressure from time to time.

* On acidifying the sodium carbonate extract, 0.8 gram of crude bornylene-3-carboxylic acid separated and melted at $106-107^\circ$.

The product is mixed with water, and extracted twice with ether*; the ethereal solution is washed and evaporated, and the residue mixed with two volumes of hydrochloric acid and well shaken during half an hour; water is then added, and the whole distilled in steam, when crude epicamphor mixed with bornylene-carboxylic acid passes over as a semi-solid mass, which frequently blocks the condenser. Ether is distilled down the condenser, the distillate extracted with ether, and the ethereal solution evaporated; the residue is warmed with methyl-alcoholic potassium hydroxide (10 grams KOH) for an hour, water is then added, and the epicamphor, which separates as a solid, extracted with ether. The ethereal solution is washed very thoroughly, dried and evaporated, when a syrup remains, which, when stirred in a current of air, soon becomes nearly solid. After contact with porous porcelain, the epicamphor, which remains as a colourless solid, is sufficiently pure for all ordinary purposes. The porous porcelain from several such operations is extracted with ether in a Soxhlet apparatus, the extract evaporated and distilled under 100 mm. pressure, and, in this way, a considerable additional quantity of pure epicamphor is obtained.

The alkaline aqueous solution is evaporated until free from ether and methyl alcohol, acidified, and the nearly pure bornylene-3-carboxylic acid which separates is collected, washed, dried on porous porcelain, and employed in a subsequent operation.

The yields obtained in this preparation vary in a manner which it is difficult to explain, but, if the operation is successful, the result should be about as follows:

Epicamphor, obtained directly	14	grams.
" recovered from plates by distillation ...	5	"
Recovered bornylenecarboxylic acid	6.9	"

The yield of epicamphor, allowing for the recovered bornylene-carboxylic acid, is therefore nearly 76 per cent. of that theoretically possible. It may be further purified by conversion into the semi-carbazone (p. 2209) and subsequent regeneration by means of hydrochloric acid:

0.2145 gave 0.6151 CO_2 and 0.2062 H_2O . $\text{C} = 78.2$; $\text{H} = 10.7$.

0.1975 " 0.5693 CO_2 " 0.1876 H_2O . $\text{C} = 78.6$; $\text{H} = 10.6$.

$\text{C}_{10}\text{H}_{16}\text{O}$ requires $\text{C} = 79.0$; $\text{H} = 10.5$ per cent.

During the purification of the crude epicamphor by distillation in steam, as described above, the liquid remaining in the steam distillation flask generally deposits colourless crystals on keeping, sometimes in considerable quantity.

These were collected and recrystallised from dilute hydrochloric

* See footnote, p. 2203.

acid, from which the substance separated in glistening plates melting at 135—137°. On investigation this substance was recognised as toluene-*p*-sulphonamide, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NH}_2$ (Found, C=48.9; H=5.3; N=8.2. $\text{C}_7\text{H}_9\text{O}_2\text{S}$ requires C=49.1; H=5.3; N=8.2 per cent.), and it is remarkable that this amide should be sufficiently stable to survive the long-continued distillation with dilute hydrochloric acid.

The Properties and Derivatives of l-Epicamphor.

l-Epicamphor melts at about 182° and distils at 213° (camphor melts at 177—178° and distils at 207°), and has a penetrating odour closely resembling and yet distinct from that of *d*-camphor. It is sparingly soluble in water, but readily so in alcohol or ether, and when placed on water it rotates like camphor. It is very readily volatile in steam. *l*-Epicamphor is laevorotatory, the value at 19° in benzene solution at a concentration of 13.1205 being $\alpha_D - 58.21^\circ$, whereas camphor, under similar conditions, has $\alpha_D + 39.1^\circ$. On reduction, *l*-epicamphor is converted into *l*-epiborneol (p. 2222), but it is comparatively stable to oxidising agents, and is scarcely attacked by cold dilute permanganate or when boiled with dilute nitric acid (D 1.25), but more concentrated acid gradually attacks it, with formation of *d*-camphoric acid. In carrying out this oxidation, epicamphor (1 gram) was heated with nitric acid (13 c.c. of D 1.3) in a sealed tube for three hours at 100°, and then for a further three hours at 115°, when, on keeping, a crystalline substance separated, and a further quantity was obtained by evaporating the acid liquid and rubbing the semi-solid residue with chloroform. The substance was recrystallised from water, and shown to be camphoric acid by the fact that it melted at 186°, yielded an anhydride melting at 222—224°, and that mixtures of these substances with ordinary camphoric acid and its anhydride exhibited no alteration in their melting points. As was to be expected, the camphoric acid obtained by the oxidation of epicamphor showed exactly the same dextrorotation as a specimen prepared from ordinary camphor.

l-Epicamphoroxime, $\text{C}_8\text{H}_{14} \begin{array}{l} \text{C:N}\cdot\text{OH} \\ | \\ \text{CH}_2 \end{array}$, may be obtained by adding sodium ethoxide and hydroxylamine hydrochloride to the alcoholic solution of *l*-epicamphor, but it is more conveniently prepared, and in almost quantitative yield, by the following process. Epicamphor (5 grams), hydroxylamine hydrochloride (4 grams), and excess of sodium acetate are digested with alcohol for an hour. On adding water, the milky liquid soon crystallises, and, after collecting, washing with water, and drying on porous porcelain, the oxime

melts at 98—100°, and is almost pure. It separates from dilute methyl alcohol at first as a milky precipitate, but this on stirring at once crystallises in glistening needles:

0.1398 gave 0.3710 CO₂ and 0.1315 H₂O. C=72.3; H=10.4.

0.2238 „ 16.8 c.c. N₂ at 22° and 760 mm. N=8.6.

0.1397 „ 10.8 c.c. N₂ „ 25° „ 758 mm. N=8.5.

C₁₀H₁₇ON requires C=71.8; H=10.2; N=8.4 per cent.

Epicamphoroxime melts at 103—104°, is very readily soluble in the usual organic solvents, and has the odour of mice so characteristic of camphoroxime. It is dextrorotatory, the solution of 0.6293 gram, made up to 10 c.c. in benzene, having $\alpha_D +100.5^\circ$. Camphoroxime is levorotatory, the solution of 0.5196 gram, made up to 10 c.c. in benzene, having $\alpha_D -56.0^\circ$.

l-Epicamphorsemicarbazone, C₈H₁₄ $\begin{matrix} \text{C:N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 \\ \text{CH}_2 \end{matrix}$.—In order

to prepare this derivative, *l*-epicamphor (7.7 grams), dissolved in alcohol, was mixed with a solution of semicarbazide hydrochloride (6.5 grams) and crystallised sodium acetate (8 grams) in water (20 grams), and boiled for one and a-half hours on the steam-bath, and then left over-night, during which the bulk of the semicarbazone (8.3 grams) had crystallised, and a further quantity (1.4 grams) was precipitated from the alcoholic solution by the addition of water. The substance was purified by recrystallisation from alcohol, from which it separated in microscopic, flat needles, which are quite different in appearance from the short prisms of camphorsemicarbazone:

0.1483 gave 0.3444 CO₂ and 0.1239 H₂O. C=63.3; H=9.3.

0.1039 „ 19 c.c. N₂ at 22° and 760 mm. N=20.7.

C₁₁H₁₉ON₃ requires C=63.2; H=9.1; N=20.1 per cent.

When rapidly heated, epicamphorsemicarbazone melts and decomposes at 237—238° (camphorsemicarbazone melts and decomposes at 247—248°); it is very sparingly soluble in water, but dissolves readily in hot methyl or ethyl alcohol. It dissolves in concentrated hydrochloric acid, and, if the solution is at once diluted with water, part separates unchanged, but when the whole is distilled in steam, the unchanged substance dissolves, decomposition rapidly takes place, and pure epicamphor distils over.

Bromo-l-epicamphor, C₈H₁₄ $\begin{matrix} \text{CO} \\ \text{CHBr} \end{matrix}$.—In order to prepare this

substance, epicamphor (3 grams) was mixed in a tube with bromine (3.5 grams) and heated in the steam-bath for two hours. The crystalline product which separated was collected, dissolved in ether, in which it is not very readily soluble, the ethereal solution washed with dilute sodium hydroxide, dried and evaporated, and the pale

brown, crystalline mass left in contact with porous porcelain until quite dry. The substance was then dissolved in light petroleum (b. p. 50—60°), and the solution concentrated, when, on cooling, groups of needles crystallised, but when the solution was allowed to concentrate spontaneously the substance separated in glistening, elongated prisms. The mother liquors were carefully examined, and yielded a further quantity of the same substance, but there was no evidence of the presence of any isomeride:

0.1488 gave 0.1198 AgBr. Br = 34.2.

$C_{10}H_{15}OBr$ requires Br = 34.6 per cent.

Bromo-l-epicamphor melts at 133—134° (bromocamphor at 76°), and dissolves readily in chloroform or benzene, but less so in alcohol; it is rather sparingly soluble in cold light petroleum, and much more readily so on warming:

0.7242, dissolved in ethyl acetate and made up to 20 c.c., had $\alpha_D - 86.6^\circ$, whereas the rotation of bromocamphor in 10 per cent. alcoholic solution is $\alpha_D + 140^\circ$.

Behaviour of l-Epicamphor in Contact with Hydrocyanic Acid.

For reasons stated in the introduction (p. 2191), the behaviour of epicamphor in contact with hydrocyanic acid was investigated under various conditions, but in no case could any signs of combination be observed; thus, in one experiment, finely-divided epicamphor (2 grams) was shaken in a stoppered bottle with pure potassium cyanide (5 grams) dissolved in a little water, and made nearly acid by the addition of acetic acid. The epicamphor liquefied, and, after twenty-four hours, the whole was extracted with ether, the ethereal solution dried and evaporated, when a solid residue of epicamphor was left, and almost the whole was recovered in this way, so that, if any combination had taken place, it must have been to a very slight extent.

The isoNitroso-l-epicamphors and Amino-l-epicamphor.

The two (α - and β -) *isonitroso-l-epicamphors* are obtained together by the action of sodamide and *isoamyl* nitrite on the ethereal solution of epicamphor under the following conditions (P., 1912, 28, 57).

Epicamphor (10 grams), dissolved in anhydrous ether (100 c.c.), is mixed with finely-powdered sodamide (4 grams), and, after two hours, freshly distilled *isoamyl* nitrite (9 c.c.) is gradually added, the temperature being kept at 0° during the addition. After remaining for twenty-four hours at the ordinary temperature, the orange-red solution is mixed with ice-water, the ethereal layer

separated, and the aqueous solution once more extracted with ether; it is then freed from ether by passing a stream of air, and acidified with acetic acid, when an oil separates in quantity, and gradually solidifies. The solid (8.5 grams) was collected, left in contact with porous porcelain over sulphuric acid in a vacuum desiccator, and then dissolved in hot light petroleum (b. p. 80—85°) with the addition of a little benzene, when, on keeping, groups of long needles separated first, and these were rapidly collected and purified by repeated recrystallisation from the same solvent:

0.1363 gave 0.3320 CO₂ and 0.1022 H₂O. C=66.4; H=8.3.

0.1156 „ 8.0 c.c. N₂ at 19° and 750 mm. N=7.8.

C₁₀H₁₅O₂N requires C=66.2; H=8.3; N=7.7 per cent.

α -isoNitroso-l-epicamphor melts at 168—170°, and dissolves readily in warm alcohol, benzene, or chloroform, and it differs from the β -modification (see below) by being much more sparingly soluble in light petroleum. It dissolves readily in dilute sodium hydroxide with a pale yellow colour, and when the solution is acidified with acetic acid it may remain clear for some time, and then gradually deposits crystals of the pure α -modification. A solution containing 0.799 in benzene, made up to 20 c.c., gave α_D -201.9°. Forster and Spinner, who obtained *α -isonitrosoepicamphor* by another process (T., 1912, 101, 1350), found the melting point to be 170° and the rotation, in chloroform, α_D -200.1°. They also prepared the benzoyl derivative (m. p. 122.5°, α_D -128.7°), the *O*-methyl ether (m. p. 100°, α_D -201.5°), and the phenylurethane (m. p. 106°, α_D -110.2°).

α -isoNitroso-l-epicamphor dissolves readily in a 40 per cent. formaldehyde solution, and if, after heating on the steam-bath for an hour, hydrochloric acid is added and the solution boiled, it at once turns yellow and deposits crystals of camphorquinone. Concentrated sulphuric acid dissolves *α -isonitrosoepicamphor*, and the solution, heated on the steam-bath for two or three minutes and then diluted with water, yields a white, crystalline precipitate, which, after recrystallisation, melts at 244—245°, and consists of the imide of *d*-camphoric acid.

β -isoNitroso-l-epicamphor.—The light petroleum mother liquors from the crystallisation of the α -derivative yielded, on slow evaporation, a small crop of crystals, which consisted of a mixture of the α - and β -isomerides, and then pale yellow prisms of the almost pure β -derivative. These were collected and further purified by fractional crystallisation from light petroleum:

0.1453 gave 0.3526 CO₂ and 0.1091 H₂O. C=66.2; H=8.4.

0.1722 „ 12.1 c.c. N₂ at 18° and 752 mm. N=8.0.

C₁₀H₁₅O₂N requires C=66.2; H=8.3; N=7.7 per cent.

β -isoNitroso-l-epicamphor melts at 138—140°, and dissolves readily in alcohol, benzene, chloroform, or light petroleum, and is also moderately soluble in boiling water. Rotation: 1.0138 dissolved in benzene and made up to 20 c.c., gave $\alpha_D - 183.5^\circ$. Forster and Spinner (T., 1912, **101**, 1349) also found that this substance melts at 140°, and they give the rotation for the solution in chloroform as -179.4° , rising to -191.4° in seven days. β -isoNitroso-l-epicamphor is converted into the α -isomeride by heating above its melting point or when its solution in water is boiled. It yields camphorquinone on treatment with formaldehyde and then with hydrochloric acid, and the imide of camphoric acid when it is heated with concentrated sulphuric acid (Claisen and Manasse, *Annalen*, 1893, **274**, 73). The benzoyl derivative (m. p. 80°, $\alpha_D - 130.0^\circ$), the *O*-methyl ether (m. p. 77°, $\alpha_D - 173.6^\circ$), and the phenylurethane (m. p. 118°, $\alpha_D - 124.3^\circ$) have been prepared by Forster and Spinner (*loc. cit.*, pp. 1349—1350).

Amino-l-epicamphor, $C_8H_{14} \begin{smallmatrix} \text{CO} \\ | \\ \text{CH} \cdot \text{NH}_2 \end{smallmatrix}$, is produced by the reduction

either of α - or β -isonitrosoepicamphor by means of zinc dust and aqueous alkali. The isonitrosoepicamphor (10 grams) is dissolved in sodium hydroxide (40 c.c. of 30 per cent.), and then zinc dust (12 grams) added in small quantities at a time, when the deep yellow colour of the solution almost completely disappears. The oily precipitate is extracted with ether, the ethereal solution dried over potassium carbonate, evaporated, and the thick syrup, which has a penetrating and most unpleasant odour, is stirred until it has completely crystallised. The mass is left in contact with porous porcelain, and then recrystallised by dissolving it in boiling light petroleum (b. p. 45—50°), and then cooling in a freezing mixture, and, since it becomes viscid and decomposes on heating, it was dried in a current of air free from carbon dioxide:

0.1425 gave 0.3749 CO_2 and 0.1281 H_2O . $C=71.7$; $H=10.0$.

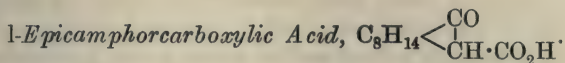
0.1917 „ 13.9 c.c. N_2 at 18° and 761 mm. $N=8.3$.

$C_{10}H_{17}ON$ requires $C=71.8$; $H=10.2$; $N=8.4$ per cent.

Amino-l-epicamphor melts at 168—170°, and is readily soluble in alcohol, ether, benzene, or light petroleum, and also in water; the solution of 0.5902 in benzene, made up to 10 c.c., gave $\alpha_D + 15.0^\circ$.

Forster and Spinner (*loc. cit.*, p. 1355) found that aminoepicamphor melted at 168—169°, and, in alcoholic solution, had $\alpha_D + 11.9^\circ$. We have not noticed that aminoepicamphor changes so rapidly as these authors seem to suggest, and specimens which have been sealed up for a year seem hardly to have altered in appearance. The discrepancy in the rotations ($\alpha_D + 30.15^\circ$ instead

of $+15.07^\circ$; compare P., 1912, **28**, 57) which Forster and Spinner seem to think may have been due to partial change of the substance into epidihydrodicamphenepyrzine, was in reality due to a mistake in our calculation, the volume of the benzene solution having been taken as 20 c.c. instead of 10 c.c. We can confirm the statement of Forster and Spinner that the α - and β -isonitroso-*l*-epicamphors both yield the same amino-*l*-epicamphor on reduction, and, therefore, in most of our experiments, the isomeric isonitroso-derivatives were not first separated, but the mixture was directly used for the reduction.



The first specimens of this acid were prepared by a method similar to that recommended for the preparation of camphorcarboxylic acid (Brühl, *Ber.*, 1891, **24**, 3384; compare Bredt, *Annalen*, 1909, **366**, 11), namely, by acting on sodium *l*-epicamphor with carbon dioxide. Thin sodium ribbon (2.2 grams) was covered with a solution of epicamphor (10 grams) in absolute ether (120 c.c.) in a double-necked flask, fitted with a very efficient condenser and a tube for the delivery of carbon dioxide, and heated on the steam-bath whilst a rapid stream of carbon dioxide was passed. The reaction commences at once, and, if care is taken not to let it slacken, the sodium will, at the end of two to three hours, have been almost completely used up; the mass is then allowed to remain over-night, and the heating and passage of carbon dioxide continued for another hour. The product is decomposed by ice, the aqueous solution separated, extracted with ether, and carefully concentrated on the steam-bath, when, on fractionally precipitating with dilute hydrochloric acid, a resinous substance first separates, and, after removing this by filtration, almost pure epicamphorcarboxylic acid separates on the further addition of the hydrochloric acid, but the yield is not more than 2 grams. The ethereal solution, on evaporation, deposited 5.1 grams of a solid, and from this, on distillation in steam, 2 grams of a substance was obtained, which melted at $177\text{--}179^\circ$, and consisted of *l*-epiborneol (p. 2222) mixed with a little epicamphor. The portion not volatile in steam contains a substance which crystallises from light petroleum in slender needles, melts at $256\text{--}257^\circ$, and is probably the pinacone of *l*-epicamphor, since it yielded the following results on analysis:

0.1657 gave 0.4743 CO_2 and 0.1683 H_2O . $\text{C}=78.1$; $\text{H}=11.3$.

$(\text{C}_{10}\text{H}_{17}\text{O})_2$ requires $\text{C}=78.4$; $\text{H}=11.2$ per cent.

Other crystalline substances of lower melting point were also present, the nature of which could not be determined.

Since the yield of epicamphorcarboxylic acid obtained by the above process was seldom more than 20 per cent. of that theoretically possible, and this loss of valuable epicamphor was serious, a long series of experiments was made first with the object of improving the method of preparation of camphorcarboxylic acid, and of then applying the process to epicamphor and with excellent results, since it is now possible to prepare epicamphorcarboxylic acid in a yield of at least 90 per cent. of that theoretically possible. This process consists in treating epicamphor with sodamide and carbon dioxide, but in benzene solution, since the reaction does not proceed with a satisfactory yield when ether is employed as the solvent.* Epicamphor (20 grams), dissolved in benzene (150 c.c.), is mixed with finely-powdered sodamide (14 grams) and heated to boiling in a two-necked flask connected with a condenser, and a rapid stream of carbon dioxide is passed through a tube which must be fitted with a wide end in order to avoid stoppage by the thick, gelatinous mass which rapidly forms. After about an hour the product is mixed with ice and water, the benzene solution separated, and the aqueous layer filtered and acidified with hydrochloric acid, when epicamphorcarboxylic acid separates in an almost pure condition, and a small quantity of less pure acid is obtained by extraction with ether. The benzene solution containing the unchanged epicamphor, and the amount of which may be approximately calculated from the weight of epicamphorcarboxylic acid resulting from the first operation, is thoroughly dried, half the benzene is removed by careful fractionation with a Young column, and the remaining solution again treated with sodamide and carbon dioxide, and this process is repeated until no more epicamphor remains in the benzene, and in this way an almost quantitative yield of epicamphorcarboxylic acid has been obtained on several occasions. The acid may be purified by contact with porous porcelain and recrystallisation from a mixture of benzene and light petroleum, from which it separates in colourless needles, but the best method is to dissolve the acid in a slight excess of sodium carbonate in a beaker fitted with a mechanical stirrer, and then to add very dilute hydrochloric acid until the small quantity of sticky impurity has been removed; after filtering, the acid obtained as a colourless precipitate on the addition of excess of hydrochloric acid is pure:

0.1937 gave 0.4473 CO_2 and 0.1444 H_2O . C=67.4; H=8.3.

0.1741 „ 0.4295 CO_2 „ 0.1295 H_2O . C=67.3; H=8.3.

$\text{C}_{11}\text{H}_{16}\text{O}_3$ requires C=67.3; H=8.2 per cent.

l-Epicamphorcarboxylic acid is rather sparingly soluble in cold

* This process may be employed with equal success in the preparation of camphorcarboxylic acid.

water, but dissolves easily in alcohol, ether, or benzene, less readily in light petroleum. Owing to the fact that this acid, like camphorcarboxylic acid, is readily decomposed on heating with elimination of carbon dioxide, the melting point is difficult to determine. The behaviour of both acids was observed on the same thermometer, when epicamphorcarboxylic acid melted at 120—122°, camphorcarboxylic acid at 125—126°. In both cases decomposition took place on slowly raising the temperature, until the contents of the wide capillary tubes solidified to very pure epicamphor and camphor, which then melted sharply at 184—184·5° and 178—179° respectively.

Rotation of l-Epicamphor Carboxylic Acid: 0·7775, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D -18\cdot5^\circ$; the rotation of *d*-camphorcarboxylic acid determined for the sake of comparison gave: 1·1615, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D +57\cdot4^\circ$.

Oxidation to Camphoric Acid.—In order to determine the position of the carboxyl group in *l*-epicamphorcarboxylic acid (compare p. 2192) a small quantity of this acid was dissolved in sodium carbonate and oxidised by permanganate.

Camphorcarboxylic acid, under these conditions, yields camphorquinone as well as camphoric acid, and epicamphorcarboxylic acid might be expected to exhibit the same behaviour, but the formation of camphorquinone could not be observed. When the oxidation was complete, the alkaline filtrate from the manganese precipitate was evaporated to a small bulk and acidified, when camphoric acid separated and was identified by the melting point (186°) and the melting point of the anhydride (222°).

α -Bromo-l-epicamphorcarboxylic Acid, $C_8H_{14} \begin{matrix} \diagup CO \\ \diagdown CHBr \cdot CO_2H \end{matrix}$ —

This substance is readily prepared by heating epicamphorcarboxylic acid (0·5 gram), dissolved in glacial acetic acid (5 c.c.) with bromine (0·6 gram) in a sealed tube in the water-bath. The change is a gradual one, but is complete in about four hours; the product is then mixed with two volumes of water, and allowed to remain for twenty-four hours. The bromo-acid which will have been deposited is collected, dissolved in dilute sodium carbonate, the solution filtered and acidified, when a voluminous mass of microcrystalline stars separate, which are collected, washed with water, and dried over phosphoric oxide:

0·1802 gave 0·1233 AgBr. Br=29·1.

$C_{11}H_{16}O_3Br$ requires Br=29·1 per cent.

α -Bromo-l-epicamphorcarboxylic acid melts, if rapidly heated, at about 145° with evolution of carbon dioxide, but it decomposes

at a considerably lower temperature if the determination is slowly carried out (α -bromocamphorcarboxylic acid melts at 112—113°). It is very sparingly soluble in water, more readily so in alcohol, and the alcoholic solution gives no coloration on the addition of ferric chloride.

When this bromo-acid is heated at 150° until the elimination of carbon dioxide is complete, a crystalline substance remains, which separates from light petroleum in plates, melts at 132—134°, and is identical with the bromo-*l*-epicamphor obtained by the direct bromination of epicamphor (p. 2210), since a mixture of the two substances melted at the same temperature as the components.



It is well known that camphorcarboxylic acid cannot be reduced by sodium amalgam under the usual conditions, and, assuming this fact to be due to the proximity of the tertiary carbon atom to the CO-group, it seemed possible that epicamphorcarboxylic acid, in which the CO-group is not attached to a tertiary carbon atom, might behave quite normally, and be readily reduced on treatment with sodium amalgam. *l*-Epicamphorcarboxylic acid (5 grams) was therefore dissolved in dilute sodium carbonate and shaken on the machine with a large excess of sodium amalgam for several hours; the alkaline solution was then decanted from the mercury, acidified, and distilled in steam, when a quantity of epicamphor passed over, showing that a good deal of the epicamphorcarboxylic acid had remained unchanged. When the residue from the steam distillation was extracted with ether, the ethereal solution left, on evaporation, only a small quantity (0.6 gram) of a gum which possibly contained epiborneolcarboxylic acids, but it is evident that epicamphorcarboxylic acid, like camphorcarboxylic acid, cannot be effectively reduced under these conditions. The acid is, however, readily reduced by means of potassium amalgam produced electrolytically in an apparatus similar to that recommended by Bredt (*J. pr. Chem.*, 1911, [ii], **84**, 792) for the reduction of camphorcarboxylic acid. The aqueous layer from this reduction of about 60 grams of epicamphorcarboxylic acid was nearly neutralised with hydrochloric acid, filtered, and then acidified, when a chalky precipitate separated, which was collected and left in contact with porous porcelain until quite dry. This represented practically the whole of the product, since ether extracted only about 2 grams from the filtrate. The chalky mass was carefully extracted with several quantities of boiling light petroleum (b. p. 80—100°) until an acid remained which melted at 168—172°. This was then twice crystallised from

boiling toluene, from which it separated as a voluminous mass of thin plates, and, when dry, had a beautiful, satiny appearance. The pure acid, which weighed 2.5 grams, melted at 173° , and is called (C)-*l-epiborneolcarboxylic acid*; the analysis and rotation of the acid are given below. The mother liquors from this acid were freed from solvent by distillation from the steam-bath under reduced pressure, the mass was dissolved in sodium carbonate, the acid again precipitated, dried, and extracted with boiling light petroleum (b. p. $60-70^{\circ}$) until the residue melted at $140-145^{\circ}$, and this, which we propose to name (B)-*l-epiborneolcarboxylic acid*, weighed 24.5 grams, and was the principal product of the reduction.

The light petroleum mother liquors were exposed to the air and allowed to concentrate spontaneously, when they next deposited 5.8 grams of curious, warty nodules melting at $120-122^{\circ}$, and these were collected and again crystallised by solution in light petroleum and spontaneous concentration, when the melting point rose to 125° , and was not altered by further crystallisation. This acid is called (A)-*l-epiborneolcarboxylic acid*. The combined light petroleum mother liquors were now allowed to concentrate very slowly in the ice-chest, and yielded 1.5 grams of an acid which softened at 230° and melted at 237° , and it is curious that this acid, although apparently the least soluble of all the isomerides, should separate after the others. This acid, for which the name (D)-*l-epiborneolcarboxylic acid* is proposed, was recrystallised from light petroleum, from which it separated in warty groups melting at 237° with decomposition and slight previous softening. The final mother liquors were evaporated, and yielded a mixture of the epiborneolcarboxylic acids, which were not separated by fractional crystallisation, but used directly for the preparation of bornylene-2-carboxylic acid (p. 2218).

Analyses and rotations of the epiborneolcarboxylic acids:

(A)-*l-Epiborneolcarboxylic Acid*, m. p. 125° .

0.1110 gave 0.2700 CO_2 and 0.0910 H_2O . $\text{C}=66.4$; $\text{H}=9.1$.

$\text{C}_{11}\text{H}_{18}\text{O}_3$ requires $\text{C}=66.7$; $\text{H}=9.1$ per cent.

0.9299, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D + 2.36^{\circ}$.

(B)-*l-Epiborneolcarboxylic Acid*, m. p. 145° .

0.1224 gave 0.2985 CO_2 and 0.1004 H_2O . $\text{C}=66.4$; $\text{H}=9.1$.

1.1046, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D - 4.8^{\circ}$.

(C)-*l-Epiborneolcarboxylic Acid*, m. p. 173° .

0.1175 gave 0.2865 CO_2 and 0.0952 H_2O . $\text{C}=66.5$; $\text{H}=9.0$.

0.2174, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D + 15.18^\circ$.

(D)-l-Epiborneolcarboxylic acid melts at 237° with evolution of gas, but without darkening, and the melted mass did not crystallise on cooling. It is almost insoluble in hot water, but dissolves readily in alcohol, boiling light petroleum (b. p. $90-100^\circ$), or in boiling toluene:

0.1452 gave 0.3555 CO_2 and 0.1134 H_2O . $\text{C} = 66.8$; $\text{H} = 8.7$.

0.1306 „ 0.3201 CO_2 „ 0.1028 H_2O . $\text{C} = 66.7$; $\text{H} = 8.7$.

0.1386, dissolved in ethyl acetate and made up to 20 c.c., had $\alpha_D + 77.9^\circ$.

$\text{C}_{11}\text{H}_{18}\text{O}_3$ requires $\text{C} = 66.7$; $\text{H} = 9.1$ per cent.

$\text{C}_{22}\text{H}_{34}\text{O}_6$ requires $\text{C} = 67.0$; $\text{H} = 8.6$ per cent. (compare p. 2193).

All the epiborneolcarboxylic acids are stable to permanganate, that is to say, their solutions in a slight excess of sodium carbonate mixed with ice do not decolorise permanganate on keeping for about a minute, and the most readily oxidisable of the isomerides appears to be the (A)-acid.

l-Bornylene-2-carboxylic Acid, $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CH} \\ | \\ \text{C} \cdot \text{CO}_2\text{H} \end{smallmatrix}$, and l-Camphane-2-carboxylic Acid, $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH} \cdot \text{CO}_2\text{H} \end{smallmatrix}$.

In preparing l-bornylene-2-carboxylic acid, the crude mixture of l-epiborneolcarboxylic acids (p. 2216, 30 grams) was mixed with acetyl chloride (150 c.c.) and heated to boiling in a reflux apparatus for fifteen hours; the excess of acetyl chloride was then distilled off, and the syrupy mass distilled under diminished pressure (15 mm.), when almost the whole passed over, and only a small, crystalline residue remained.

The syrupy distillate and the residue were dissolved in methyl alcohol (200 c.c.) and sulphuric acid (15 c.c.), and, after remaining over-night, the whole was heated in a reflux apparatus for one hour; water was then added, and the oily methyl ester extracted with ether.

The ethereal solution was well washed with sodium carbonate, dried, evaporated, and the oil twice distilled under diminished pressure, when almost the whole quantity passed over at $155^\circ/100$ mm.:

0.1668 gave 0.4533 CO_2 and 0.1410 H_2O . $\text{C} = 74.1$; $\text{H} = 9.4$.

$\text{C}_{12}\text{H}_{18}\text{O}_2$ requires $\text{C} = 74.2$; $\text{H} = 9.3$ per cent.

0.6596, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D - 95.7^\circ$, but this value must not be taken as the true rotation of this methyl ester.

The *methyl 1-bornylene-2-carboxylate* thus obtained (25 grams) was hydrolysed by boiling for an hour with methyl-alcoholic potassium hydroxide (KOH=20 grams); water was added, the solution nearly neutralised with hydrochloric acid, and the methyl alcohol removed by evaporation. When the filtered solution was acidified, a syrup separated, which soon crystallised, and, after remaining in contact with porous porcelain until dry, the acid was further purified by recrystallisation from dilute acetone or formic acid, or it may be distilled in steam, with which, however, it passes over somewhat slowly:

0.1386 gave 0.3715 CO_2 and 0.1107 H_2O . $\text{C}=73.1$; $\text{H}=8.9$.

0.1471 „ 0.3922 CO_2 „ 0.1166 H_2O . $\text{C}=72.7$; $\text{H}=8.9$.

$\text{C}_{11}\text{H}_{16}\text{O}_2$ requires $\text{C}=73.3$; $\text{H}=8.9$ per cent.

0.5161, dissolved in ethyl acetate and made up to 20 c.c., gave

$\alpha_D - 98.82^\circ$.*

l-Bornylene-2-carboxylic acid melts at 115° , and is readily soluble in alcohol, benzene, light petroleum, ether, or acetic acid, but very sparingly so in water, and crystallises from dilute acetic acid in irregular plates.

The solution of the sodium salt decolorises permanganate, although not instantaneously.

Oxidation.—*l-Bornylene-2-carboxylic acid* is quickly oxidised by nitric acid, and, in studying this oxidation, the pure acid (0.5 gram) was warmed with nitric acid (25 c.c. of D 1.24) in a reflux apparatus, when a vigorous reaction set in, and some of the acid distilled with the nitric acid and crystallised in the condenser. After boiling for an hour a further quantity (15 c.c.) of the same acid was added, and the boiling continued for twelve hours; the product was then repeatedly evaporated with the addition of water, and the crystalline mass extracted with chloroform. The residue separated from water in glistening plates melting at 185° , and, on titration, 0.0894 neutralised 9.03 c.c. $N/10\text{-NaOH}$, whereas this amount of a dibasic acid, $\text{C}_{10}\text{H}_{16}\text{O}_4$, should neutralise 8.94 c.c. $N/10\text{-NaOH}$. Since the acid yielded an anhydride melting at $216\text{--}218^\circ$, there can be no doubt that it was *d-camphoric acid*.

l-Camphane-2-carboxylic Acid.—This acid is readily obtained by reducing bornylene-2-carboxylic acid, in dilute methyl-alcoholic solution, with hydrogen in the presence of palladium and gum arabic under the conditions already described in the case of the corresponding reduction of bornylene-3-carboxylic acid to camphane-3-carboxylic acid (p. 2199).

The product was distilled in steam, the distillate made alkaline

* The rotation of *d-bornylene-3-carboxylic acid*, in benzene solution, at a concentration of 13.1506 is $\alpha_D + 149.5^\circ$.

with sodium carbonate, evaporated until free from methyl alcohol, mixed with powdered ice and a little permanganate, and allowed to remain for an hour, but the addition of hydrogen had evidently been practically complete, since there was hardly any reduction of the permanganate.

After the removal of the permanganate, the acid was precipitated by hydrochloric acid, washed well, and dried on porous porcelain.

Owing to the fact that it is so very soluble in the usual organic solvents, the recrystallisation of this acid is a matter of difficulty, and the best plan seems to be to dissolve it in warm dilute acetic acid, and then to cool the solution below 0°, when the pure acid separates well in long, colourless needles, which are collected on a filter surrounded by a freezing mixture:

0.1343 gave 0.3560 CO₂ and 0.1198 H₂O. C=72.3; H=9.9.

C₁₁H₁₈O₂ requires C=72.5; H=9.9 per cent.

0.7489, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D - 37.8^\circ$.

l-Camphane-2-carboxylic acid melts at 78–80°, and distils at about 155°/15 mm.; it is very sparingly soluble in cold, but dissolves somewhat in boiling water, and separates, on cooling, in glistening needles.

It is mentioned on p. 2194 that this acid had already been prepared by Houben and Kesselkaul (*Ber.*, 1902, **35**, 3696; compare Houben, *Ber.*, 1905, **38**, 3799), who named it “hydropinenecarboxylic acid,” and state that it melts at 72–74°, and by Zelinsky (*Ber.*, 1902, **35**, 4417), who gives the melting point 69–71°, and called it “camphanecarboxylic acid.”

Conversion of l-Bornylene-2-carboxylic Acid into d-Camphor.

The interesting conversion of *l*-bornylene-2-carboxylic acid—and indirectly of epicamphor—into camphor was brought about through the agency of *l*-bornylene-2-hydroxamic acid (compare p. 2206). Hydroxylamine hydrochloride (12 grams), carefully dried and powdered, was dissolved in anhydrous methyl alcohol (100 c.c.), and mixed in the cold with a solution of sodium (3.5 grams) in methyl alcohol. Methyl *l*-bornylene-2-carboxylate (30 grams) was then added, and afterwards sodium (3.5 grams) dissolved in methyl alcohol (50 c.c.), and the whole allowed to remain for two days, during which no crystallisation of the sodium salt of the hydroxamic acid took place. After heating for four hours in a thermostat at 50° the product was divided into the halves (A) and (B). The portion (A) was mixed with water, a small quantity of unchanged ester (1.5 grams) extracted with ether, the aqueous solution was just acidified with hydrochloric acid and extracted three times with ether, and,

after washing well, drying, and evaporating carefully, the ethereal solution deposited a syrup which did not crystallise. This syrupy acid, which gave an intense claret coloration when ferric chloride was added to its alcoholic solution, was dissolved in a slight excess of potassium hydroxide, and the pale blue copper salt precipitated by the addition of excess of copper acetate; the precipitate was washed, dried, suspended in ether, and decomposed by hydrogen sulphide. After filtering, the ethereal solution yielded, on evaporation, an almost colourless syrup, which did not crystallise even after several days' exposure over sulphuric acid, but analysis indicated that this syrup was practically pure *l-bornylene-2-hydroxamic acid*:

0.1480 gave 9.1 c.c. N_2 at 17° and 755 mm. $N=7.2$.

$C_{11}H_{17}ON_2$ requires $N=7.2$ per cent.

Conversion of l-Bornylene-2-hydroxamic Acid into d-Camphor by Heat.—This conversion was brought about by heating the syrupy hydroxamic acid in a reflux apparatus at about 120° , when decomposition commenced and continued, after the flame had been removed, so vigorously that the temperature rose to about 200° ; a good deal of ammonia was formed, and some camphor crystallised in the neck of the flask and in the condenser. The product was mixed with concentrated hydrochloric acid and distilled in steam, and the semi-solid mass, which smelt strongly of camphor, was extracted with ether. The ethereal solution yielded, on evaporation, a buttery mass, which was left for some hours in contact with methyl-alcoholic potassium hydroxide ($KOH=5$ grams)*; water was then added, and the crystalline precipitate extracted with ether.

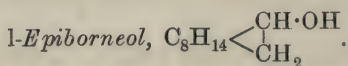
After washing thoroughly, the ethereal solution was dried and carefully evaporated, when a nearly solid mass remained, which, in contact with porous porcelain, became quite dry, and consisted of nearly pure *d*-camphor, a fact which was proved by recrystallising it from a little very light petroleum (b. p. $35-40^\circ$), when it melted at $174-176^\circ$, had $\alpha_D +46.9^\circ$ in ethyl acetate solution, and yielded camphoroxime melting at 119° .

Conversion of l-Bornylene-2-hydroxamic Acid into d-Camphor with the Aid of Toluene-p-sulphonyl Chloride.—The second portion (B) of the solution of the sodium salt of *l*-bornylene-2-hydroxamic acid, obtained as described above, was mixed with twice its volume of water, and shaken for twelve hours on the machine with finely-powdered toluene-*p*-sulphonyl chloride (25 grams). The product was extracted with ether, the ethereal solution washed, dried, and

* The alkaline solution, after the methyl alcohol has been removed by evaporation, yielded, on acidifying, crude bornylene-2-carboxylic acid (2 grams),

evaporated, and shaken for half an hour with concentrated hydrochloric acid. Water was then added, and the whole distilled in steam, when a semi-solid mass passed over, and a brown button and some crystals containing nitrogen and sulphur were left in the distillation flask (compare p. 2208). The distillate was extracted with ether, the ethereal solution evaporated, and the residual crude camphor mixed with methyl-alcoholic potassium hydroxide (5 grams KOH) and warmed on the steam-bath for half an hour in order to hydrolyse some bornylene-2-carboxylic ester which was present. Water was then added, the camphor extracted with ether, the ethereal solution very thoroughly washed, dried, and evaporated, and the *d*-camphor left on porous porcelain until quite dry, and then twice recrystallised from light petroleum (b. p. 30–40°). It was then quite pure, since it melted at 176°, and, when treated with hydroxylamine under the conditions given on p. 2208, yielded camphoroxime melting at 119°. Furthermore, there was no alteration in melting point when these preparations were mixed with ordinary *d*-camphor, which had been recrystallised from light petroleum, and with *d*-camphoroxime. The determination of the rotation gave the following result: 0.4002, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D + 47.7^\circ$, whereas the rotation of ordinary *d*-camphor, after crystallisation from light petroleum, was $\alpha_D + 48.0^\circ$ under the same conditions.

The yield of camphor obtained in the above experiment was more than 40 per cent. of that theoretically possible.



In order to obtain this substance, *l*-epicamphor, dissolved in ten times its weight of ethyl alcohol, was reduced, in a reflux apparatus, with an equal weight of sodium, which was added as rapidly as possible in order that the whole might pass into solution. If any sodium remains it is removed by the addition of ice; the whole is then distilled in steam, when the epiborneol passes over much in the same way, but not so readily, as epicamphor, and a considerable portion solidifies in the condenser, and must be removed from time to time by solution in ether.

The ethereal solution is combined with the ether extract of the distillate, washed thoroughly with water to remove the alcohol, dried, and evaporated, when *l*-epiborneol remains as a crystalline mass, which melts at 179–181°, and, after purification with the aid of the phenylurethane, at 181–182.5°:

0.1550 gave 0.4415 CO₂ and 0.1695 H₂O. C=77.7; H=12.2.

0.1392 „ 0.3975 CO₂ „ 0.1495 H₂O. C=77.8; H=11.9.

C₁₀H₁₈O requires C=77.9; H=11.7 per cent.

It is remarkable that all the specimens of *l*-epiborneol which we have obtained have proved to be inactive.

The *phenylurethane*, C₁₀H₁₇·O·CO·NH·C₆H₅, was prepared by dissolving epiborneol (6 grams) in a little light petroleum (b. p. 35—40°), adding phenylcarbimide (5 grams), and allowing the mixture to remain for several days in a sealed tube, during which some of the phenylurethane separated in white crystals, and the addition of more light petroleum precipitated a further quantity of the same substance:

0.1607 gave 0.4402 CO₂ and 0.1238 H₂O. C=74.7; H=8.6.

0.1910 „ 9.4 c.c. N₂ at 17.5° and 733.5 mm. N=5.5.

C₁₇H₂₃O₂N requires C=74.7; H=8.5; N=5.1 per cent.

l-Epibornylphenylurethane separates from light petroleum in groups of long needles, and melts at 82°; it is readily decomposed by distillation with dilute hydrochloric acid, and pure epiborneol passes over with the condensed water.

Preparation of l-Epiborneol from Sodium l-Epibornylxanthate.

When sodium epibornylxanthate (see below) is dissolved in hot water and mixed with hydrochloric acid a precipitate of epiborneol is at once produced, and, after distilling in steam, extracting with ether, and evaporating, the solid was recrystallised from light petroleum several times, but the melting point remained constant at 176—176.5°, whereas the substance obtained from *l*-epicamphor by reduction with sodium and alcohol had melted at 181—182.5°:

0.1822 gave 0.5176 CO₂ and 0.191 H₂O. C=77.5; H=11.7.

C₁₀H₁₈O requires C=77.9; H=11.7 per cent.

It was at first thought that these two substances were stereoisomeric, and corresponded with borneol and isoborneol, which, as is well known, occur together in the product of the reduction of camphor. That this is probably not the case is indicated by the fact that both preparations were inactive, and that, in spite of the difference in melting points, both gave the same phenylurethane.

Conversion of l-Epiborneol into l-Bornylene by the Method of Tschugaev.

This interesting conversion of inactive *l*-epiborneol into active *l*-bornylene was carried out under the following conditions: In the first place, sodium epibornylxanthate was prepared by adding sodium ribbon (3 grams) to the solution of *l*-epiborneol (15 grams)

in absolute ether (150 c.c.) in a flask protected from moisture and carbon dioxide by a calcium chloride and soda-lime tube, when a slow and regular evolution of hydrogen set in, and was complete after remaining over-night. The unchanged sodium ribbon was easily removed, and the solution of sodium borneol was then mixed with carbon disulphide (15 grams), when a yellow precipitate separated immediately and the contents of the flask became nearly solid. The precipitate of sodium *l*-epibornylxanthate was collected and recrystallised from water, when about 70 per cent. separated as a very pale yellow, almost white, crystalline mass, and, from the mother liquors, epiborneol was recovered by treatment with hydrochloric acid. The sodium salt was converted into methyl *l*-epibornyl-

xanthate, $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CH} \cdot \text{O} \cdot \text{CS}_2\text{Me} \\ | \\ \text{CH}_2 \end{smallmatrix}$, by suspending it in ether, adding

methyl iodide, and boiling in a reflux apparatus, the whole being repeatedly shaken to ensure complete decomposition. After ten hours the product was mixed with water, the ethereal solution dried and evaporated, when the methyl ester remained as a rather mobile, yellow oil.

This oil was now heated in a small distillation flask by means of a small flame, and the gases evolved (methyl mercaptan and carbonyl sulphide) ignited, so that the progress of the decomposition could be judged by the size of the jet. After a short time bornylene commenced to distil over, and crystallised in the receiver as a colourless mass. The distillation was repeated, and the *l*-bornylene then distilled over sodium, when it melted sharply at 113–114°, but did not exhibit constant rotation, since different portions of the distillate had values varying between $\alpha_D - 16.93^\circ$ and -19.58° . After a further distillation over sodium, the solution of two different specimens in benzene gave the values:

Melting point.	Concentration.	α_D .
113–114°	4.771	-18.45°
114.5–115	4.345	-18.41

Oxidation.—In carrying out this experiment, the above *l*-bornylene (2 grams) was dissolved in benzene and shaken with 700 c.c. of 1 per cent. permanganate on the machine for twenty hours; the excess of permanganate was then decomposed by sulphur dioxide, and the filtrate and washings from the manganese precipitate concentrated, acidified, and the precipitated acid extracted with ether. After distilling off the ether, the mass was boiled with chloroform, decanted, and the residue recrystallised from water, when an acid was obtained, which melted at 188°, and proved on examination to consist of pure *d*-camphoric acid.

l-Bornylene had been previously obtained by Bredt (*Annalen*,

1909, **366**, 52) by the decomposition of sodium β -bromodihydro-bornylene-3-carboxylate (compare p. 2191), and was found to have the constants: m. p. 113° ; b. p. 146° ; rotation, in toluene solution at a concentration of 10.45, $\alpha_D - 21.69^{\circ}$. More recently, Tschugaev and Budrick (*Annalen*, 1912, **388**, 288) prepared *d*-bornylene from methyl *l*-bornylxanthate (from *l*-borneol) by heating at 176 — 177° , and this specimen melted at 109 — 109.5° , distilled at $146.5^{\circ}/750$ mm., and, in toluene solution at a concentration of 12.75, had $\alpha_D + 19.29^{\circ}$.

On oxidation with permanganate it yielded *l*-camphoric acid.

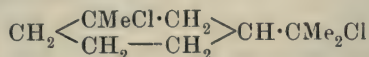
ORGANIC LABORATORY OF THE KÖNIGL.
TECHNISCHEN HOCHSCHULE-AACHEN.

THE UNIVERSITIES OF
OXFORD AND MANCHESTER.

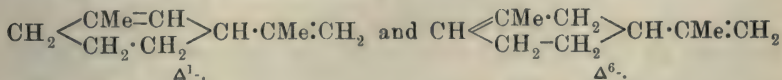
CCXXXII.—*Synthesis of d- and l-Sylvestrene.*

By WALTER NORMAN HAWORTH and WILLIAM HENRY PERKIN, jun.

d-SYLVESTRENE—that important terpene which Atterberg discovered in Swedish oil of turpentine in 1877 (*Ber.*, **10**, 1202; 1878, **11**, 1698), and which Baeyer (*Ber.*, 1894, **27**, 3488; 1898, **31**, 1067) first showed to be a derivative of *m*-cymene—is isolated from the Swedish oil in the form of the dihydrochloride, a highly characteristic derivative which melts at 72° and has $\alpha_D + 22.6^{\circ}$. The constitution of this dihydrochloride has been proved to be that represented by the formula:



(compare this vol., p. 1230), and *d*-sylvestrene is prepared by heating it with substances, such as diethylaniline, which serve to remove two molecules of hydrogen chloride. In a recent communication (this vol., p. 1232), Haworth, Perkin, and Wallach have shown that the terpene thus obtained is not a single substance, but is probably a mixture mainly of the Δ^1 - and Δ^6 -isomerides:

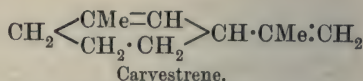
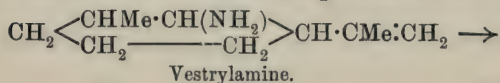


elimination of hydrogen chloride within the ring taking place in two directions, and there is also reason to believe that other isomeric substances, of the terpinolene class, are present in small quantity.

l-Sylvestrene is practically unknown, since the only mention of

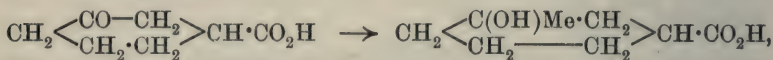
this substance appears in a paper by A. More (T., 1899, **75**, 718), who, by distilling the oil obtained from the oleo-resin of *Dacryodes hexandra*, obtained a lævorotatory oil which distilled at 173—176°, and yielded a dihydrochloride melting at 71°; its rotation was not determined, but it exhibited the characteristic crystalline form of sylvestrene dihydrochloride. Unfortunately, the amount of material available was insufficient for further investigation.

dl-Sylvestrene (carvestrene) was first prepared by Baeyer (*Ber.*, 1894, **27**, 3486; compare also *Ber.*, 1898, **31**, 1402; and T., 1907, **91**, 481) from carone by conversion into vestrylamine, the hydrochloride of which decomposes, on distillation, into ammonium chloride and carvestrene, a process which Baeyer represented thus:

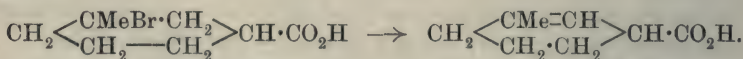


During the course of a series of experiments, made with the object of synthesising sylvestrene and its derivatives, the first positive result was the synthesis of *dl*-sylvestrene (T., 1907, **91**, 482), by a long process of which, for the purposes of the present communication, it will be necessary to call attention only to the following stages.

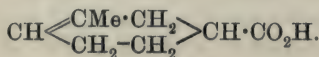
The ester of *cyclohexanone*-3-carboxylic acid is converted by treatment with magnesium methyl iodide into 1-methyl*cyclohexan*-1-ol-3-carboxylic acid:



from which, by the action of hydrobromic acid, 1-bromo-1-methyl*cyclohexane*-3-carboxylic acid was obtained, and this, when heated with pyridine, was decomposed, with elimination of hydrogen bromide and formation of 1-methyl- Δ^1 -*cyclohexene*-3-carboxylic acid:



That the acid of this constitution was formed was proved conclusively by the fact that adipic acid was obtained on oxidation, and at that time it was thought that the elimination of hydrogen bromide had taken place entirely in the direction of the carboxyl group, and that the unsaturated acid did not contain any of the Δ^6 -isomeride:



The next development was the synthesis of *d*-sylvestrene, and the first step in this was the resolution of the acid, obtained in the manner described above, by means of brucine, when an acid was obtained which had $\alpha_D + 90.8^\circ$, and subsequently $+108^\circ$, and this was assumed to be pure *d*-1-methyl- Δ^1 -cyclohexenecarboxylic acid (P., 1910, **26**, 97).*

When the ester of this acid was treated with magnesium methyl iodide, it yielded a *d*-dihydrocarvestrenol (*d*-sylveterpineol), which was thought to be pure *d*- Δ^1 -*m*-menthenol(8), and this, on treatment with hydrochloric acid, was converted into *d*-sylvestrene dihydrochloride, which melted at 72° , had $\alpha_D + 22.5^\circ$, and was identical in all respects with a specimen of the dihydrochloride which had been prepared from Swedish oil of turpentine.

When this dihydrochloride was decomposed by diethylaniline, it yielded a specimen of *d*-sylvestrene, which distilled at $174\text{--}176^\circ$, and had $\alpha_D + 67.5^\circ$, and thus the synthesis of *d*-sylvestrene was accomplished.

The most remarkable characteristic of the *d*-sylveterpineol obtained as the result of the above series of reactions was the fact that the first specimen was apparently without rotation, but a second specimen, which Prof. Pope kindly examined, had the small laevorotation $\alpha_D - 2.7^\circ$.

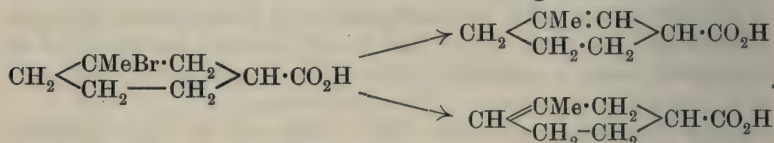
When the acid, recovered from the mother liquors of the brucine salt of the acid of $\alpha_D + 108^\circ$, was systematically treated with *l*-menthylamine, an acid of rotation $\alpha_D - 49.7^\circ$ was ultimately separated.

The ester of this acid was prepared, and yielded, on treatment with magnesium methyl iodide in the usual manner, an *l*-sylveterpineol, which had $\alpha_D - 45.9^\circ$, and this, in contact with hydrochloric acid, was converted into a dihydrochloride, which melted at 72° , had $\alpha_D - 22.1^\circ$, and was therefore obviously *l*-sylvestrene dihydrochloride. When this dihydrochloride was treated with diethylaniline, it yielded *l*-sylvestrene, which distilled at $175\text{--}178^\circ$ and had $\alpha_D - 66.5^\circ$, and in this way the synthesis of *l*-sylvestrene was accomplished. It was also interesting to observe that, when equal weights of *d*- and *l*-sylvestrene dihydrochlorides were mixed and the product recrystallised from methyl alcohol, the crystals which separated melted sharply at 52° , and consisted of pure carvestrene dihydrochloride.

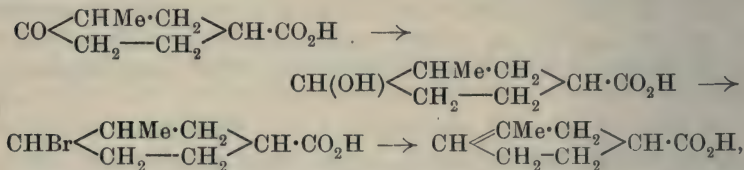
The experiments which have just been described make it quite clear that the acid obtained by the elimination of hydrogen bromide from 1-bromo-1-methylcyclohexane-3-carboxylic acid (com-

* By an unfortunate mistake in the calculation, the rotation of this acid is erroneously given here as $\alpha_D + 70^\circ$.

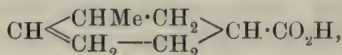
pare 2226) could not have been a single substance, but must have consisted of a mixture of *dl*-acids, the rotations of the active constituents of which are approximately represented by the values α_D 108° and 49·7°, and of these the latter was always present in by far the larger quantity. Since both of these acids ultimately lead to sylvestrene dihydrochloride, it is obvious that the one must be 1-methyl- Δ^1 -cyclohexene-3-carboxylic acid, and the other the corresponding Δ^6 -isomeride, and the possibility of the formation of these from the bromo-acid is clear from the following scheme:



In order to discover which of these acids corresponded with the rotation α_D 108° and which with that of α_D 49·7°, the following series of experiments was undertaken. 1-Methyl- Δ^6 -cyclohexene-3-carboxylic acid had been prepared by Fisher and Perkin (T., 1908, **93**, 1878) by another series of reactions, namely, from 1-methylcyclohexan-6-one-3-carboxylic acid, by reduction, conversion into the bromo-acid and subsequent elimination of hydrogen bromide:



and it seemed probable at the time, not only that the acid obtained had this constitution, but that it was free from the Δ^5 -isomeride:



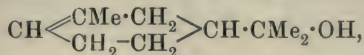
which might conceivably have been produced during the above process of preparation. In the present communication (p. 2230) oxidation experiments are described which clearly demonstrate these points. A large quantity of this acid (210 grams) was prepared and resolved by means of brucine and *l*-menthylamine, and, after an unusually laborious series of fractional crystallisations, the *d*-acid was obtained with the rotation α_D +108°, and the *l*-acid with α_D -98·6°. When the ester of the *d*-acid was treated with magnesium methyl iodide, it yielded *d*- Δ^6 -*m*-menthenol(8), which had the small levorotation α_D -2·7°, and, in contact with hydrochloric acid, was converted into *d*-sylvestrene dihydrochloride, which melted at 72°, and had α_D +22·5°, and this, on

treatment with diethylaniline, gave a specimen of *d*-sylvestrene, which distilled at 175—178°, and had $\alpha_D + 67.5^\circ$.

A similar series of experiments with the *l*-acid of rotation $\alpha_D - 98.6^\circ$ gave *l*-sylvestrene dihydrochloride (m. p. 70—72°; $\alpha_D - 21.8^\circ$), and from this, *l*-sylvestrene, boiling at 176—178° and having $\alpha_D - 68.2^\circ$, was isolated. It is thus conclusively proved that the rotation $\alpha_D 108^\circ$ is the characteristic of 1-methyl- Δ^6 -cyclohexene-3-carboxylic acid, and therefore that the rotation of the Δ^1 -acid must be represented approximately by the value $\alpha_D 49.7^\circ$.

If further proof were necessary, it was obtained by submitting the acid of rotation $\alpha_D - 49.7^\circ$ to oxidation, when it yielded adipic acid (p. 2236).

The *l*- Δ^1 -acid yielded a *l*- Δ^1 -*m*-menthenol(8), which exhibited the rotation -45.9° , a value which, except that it is of opposite sign, is identical with that observed in the case of a specimen of sylveterpineol which had been obtained by the action of potassium hydroxide on *d*-sylvestrene dihydrochloride (this vol., p. 1234). But there can be little doubt that the *d*-sylveterpineol obtained from the dihydrochloride in this way contains a certain, although probably small, quantity of *d*- Δ^6 -*m*-menthenol(8):



and, as it is shown in the present communication that the *d*- Δ^6 -isomeride has a slight levorotation of about $\alpha_D - 2.7^\circ$, its presence must reduce the rotation of the *d*- Δ^1 -isomeride, the true value of which is therefore probably somewhat higher than $\alpha_D + 45.9^\circ$.

It was pointed out on another occasion (T., 1911, **99**, 559) that, probably owing to their feebly acidic properties and to the tendency of the constituents of their salts with active bases to separate from solvents as isomorphous mixtures or mixed crystals, the resolution of the cyclohexene acids is a most laborious process, and the operations described in the present communication required more than two years to complete. It was therefore found impossible to carry the resolution of the Δ^1 -acid to a further stage, and this, although no doubt desirable, was actually not necessary, since the acids obtained were readily converted into optically pure specimens of *d*- and *l*-sylvestrene and their hydrochlorides.

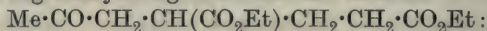
EXPERIMENTAL.

Oxidation of dl-1-Methyl- Δ^6 -cyclohexene-3-carboxylic Acid.

In the previous paper describing this acid (T., 1908, **93**, 1885) no definite proof was offered that the acid obtained, and also used

in the present research, did actually contain the double linking in the Δ^6 -position. In order to supply this proof, the acid was oxidised with ozone and then with permanganate and hypobromite under the following conditions: Ozonised oxygen was first passed through the solution of the acid (10 grams) in sodium carbonate until it was no longer absorbed, and the solution was then treated with permanganate at 0° until the pink colour remained for five minutes. The filtrate and washings from the manganese precipitate were evaporated to a small bulk, acidified, and extracted several times with ether on the machine, when a large yield of a syrupy acid was obtained, which, since it showed no signs of crystallising, was completely esterified by digesting with alcohol (70 c.c.) and sulphuric acid (5 c.c.) in a reflux apparatus for five hours. Water was then added, the ester extracted with ether, the ethereal solution thoroughly washed with water and dilute sodium carbonate, dried, evaporated, and distilled, when about 20 per cent. passed over below 170° and the remainder constantly at $175^\circ/18$ mm.

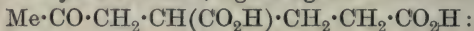
The following analysis agreed with the formula



0.1189 gave 0.2567 CO_2 and 0.0910 H_2O . $\text{C}=58.9$; $\text{H}=8.6$.

$\text{C}_{12}\text{H}_{20}\text{O}_5$ requires $\text{C}=59.0$; $\text{H}=8.2$ per cent.

This ester was digested with dilute hydrochloric acid (5 per cent.) for ten hours; the whole was then evaporated to complete dryness, by distillation from the water-bath under a pressure of 15 mm., and the nearly colourless syrup left over powdered potassium hydroxide in a vacuum desiccator and constantly stirred until it contained only a trace of hydrochloric acid. This substance yielded the following analytical results, agreeing with the formula



0.1446 gave 0.2389 CO_2 and 0.0845 H_2O . $\text{C}=50.7$; $\text{H}=6.5$.

$\text{C}_8\text{H}_{12}\text{O}_5$ requires $\text{C}=51.1$; $\text{H}=6.4$ per cent.

Titration: 0.4142 requires, for neutralisation, 44.9 c.c. $N/10$ -NaOH, whereas this amount of a dibasic acid, $\text{C}_8\text{H}_{12}\text{O}_5$, should neutralise 44.1 c.c. $N/10$ -NaOH.

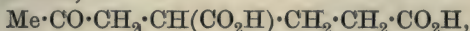
Oxidation of the Acid, $\text{C}_8\text{H}_{12}\text{O}_5$, by means of Sodium Hypobromite.—In this experiment sodium hydroxide (8 grams), dissolved in water (50 c.c.) and powdered ice (about 100 grams), was gradually mixed with bromine (10 grams), and then the solution of the dibasic acid, $\text{C}_8\text{H}_{12}\text{O}_5$ (7.5 grams), in a slight excess of sodium hydroxide was rapidly added with vigorous mechanical stirring. In a short time the separation of bromoform was complete, and, after remaining for an hour, the bromoform (about 3 grams) was run off, the solution acidified with sulphuric and sulphurous acids,

saturated with ammonium sulphate, and extracted five times with much ether on the machine. The well-dried ethereal solution deposited, on evaporation, a syrup which gradually crystallised, and, after remaining in contact with porous porcelain until quite dry, the acid was recrystallised from acetone, from which it separated in lustrous prisms:

0.1307 gave 0.2116 CO_2 and 0.0634 H_2O . $\text{C}=44.1$; $\text{H}=5.4$.

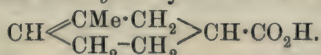
$\text{C}_7\text{H}_{10}\text{O}_6$ requires $\text{C}=44.2$; $\text{H}=5.3$ per cent.

That this acid, which melted at $117-118^\circ$, was butane- $\alpha\beta\delta$ -tricarboxylic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, was confirmed by the fact that, when it was mixed with a specimen of this acid which had previously been obtained synthetically by Kay and Perkin (T., 1906, **89**, 1644), there was no alteration in melting point. It is therefore clear that the product of the oxidation of the unsaturated acid by ozone and permanganate is *hexan- ϵ -one- $\alpha\gamma$ -dicarboxylic acid*,



and the formation of this acid proves that the *dl*-acid employed in this series of oxidations is *dl*-1-methyl- Δ^6 -cyclohexene-3-carboxylic acid. The porous porcelain which had been employed in the purification of the crude butanetricarboxylic acid was extracted with ether in a Soxhlet apparatus, and the small quantity of syrupy acid dissolved in a little concentrated hydrochloric acid and allowed to remain over powdered potassium hydroxide for some days with frequent stirring, when it deposited a further small quantity of the same acid, and there was no evidence of the presence of any other substance.

Resolution of dl-1-Methyl- Δ^6 -cyclohexene-3-carboxylic Acid,



Several active bases were employed in the preliminary experiments on the resolution of this acid, but ultimately advantage was more particularly taken of the brucine salts and the salts with *l*-menthylamine, and, as illustrations of the methods employed, the following experiments only will be described in detail:

I.—*Isolation of d-1-Methyl- Δ^6 -cyclohexene-3-carboxylic Acid by means of Brucine. Method I.*—The *dl*-acid (50 grams), dissolved in ethyl acetate, was mixed with rather more than half the quantity of brucine required for neutralisation (75 grams), dissolved in ethyl acetate, the solution was then well shaken with small quantities of water until a few drops remained undissolved,* and

* In all these resolutions it was found that, whereas the brucine salts crystallise with difficulty and then very imperfectly from dry ethyl acetate, the crystallisation is much facilitated when the solvent is saturated with water.

allowed to remain in the ice-chest, when a thick crust of crystals soon separated, and these were collected and four times recrystallised from ethyl acetate. The salt was then decomposed by sodium carbonate, the brucine collected, washed, and the alkaline solution concentrated, acidified, and extracted with ether, when 5 grams of acid were obtained, which, after distillation, had $\alpha_D + 59.7^\circ$.*

Method II.—The *dl*-acid (14 grams) was exactly neutralised with *N*/10-sodium hydroxide, heated to boiling, and then an alcoholic solution containing brucine (60 grams) and the *dl*-acid (14 grams) was added, and the whole evaporated nearly to dryness. When the syrupy residue was vigorously stirred with water, crystallisation was gradually induced, and, after remaining in the ice-chest for several days, the pasty mass was transferred to the pump, washed with a little ice-water, and dissolved in boiling water, in which it was readily soluble. The felted mass of needles, which separated on cooling, was several times recrystallised from water, during which operation it was noticed that the salt became gradually less soluble and more granular in appearance.

The salt was then decomposed in the usual manner, and yielded 3.5 grams of an acid which distilled at $138\text{--}140^\circ/18\text{ mm.}$, and had $\alpha_D + 108^\circ$, and as, in a subsequent experiment, more frequent crystallisation of the brucine salt did not produce any rise in the rotation, it is assumed that $\alpha_D + 108^\circ$ is the true rotation of *d*-1-methyl- Δ^6 -cyclohexene-3-carboxylic acid.

II.—Isolation of 1-1-Methyl- Δ^6 -cyclohexene-3-carboxylic Acid by means of l-Menthylamine.—After the brucine salt of the *d*-acid had been removed as completely as possible by the repeated application of the methods just described, the acid was recovered from the mother liquors, distilled, and then systematically treated with *l*-menthylamine, and the following experiment may be described as an example of this treatment. The *l*-acid of rotation $\alpha_D - 17.6^\circ$ (50 grams) was dissolved in *N*-sodium hydroxide (365 c.c.), heated to boiling, and then a hot solution of *l*-menthylamine hydrochloride (75 grams) was added all at once with vigorous stirring, when an oily layer separated at the surface, and, on remaining in the ice-chest for a few days, this became a thick paste of crystals. The aqueous solution, after decanting and filtering, yielded about 7 grams of acid, which was nearly inactive, and the pasty menthylamine salt was left in contact with porous porcelain until quite dry. After twice recrystallising from methyl ethyl ketone, the salt yielded, on decomposition with sodium carbonate, an acid which, after distillation, had $\alpha_D - 32.5^\circ$, and

* The concentration employed in all the determinations mentioned in this communication was roughly 5 per cent., and the solvent was always ethyl acetate.

by repeating this treatment with *l*-menthylamine a large number of times both with this acid of rotation -32.5° and with the acid which was absorbed as *l*-menthylamine salt by the porous plates, a specimen (11 grams) of *l*-1-methyl- Δ^6 -cyclohexene-3-carboxylic acid was obtained, which had the rotation $\alpha_D -98.6^\circ$ instead of the rather higher value $\alpha_D -108^\circ$, which would correspond with the highest value observed in the case of the *d*-acid.

Synthesis of d- and l-Sylvestrene.

In the synthesis of *d*-sylvestrene, *d*-1-methyl- Δ^6 -cyclohexene-3-carboxylic acid (12 grams; $\alpha_D +108^\circ$) was converted into the ester by means of alcoholic sulphuric acid in the usual manner, and the ester was then added to an ethereal solution of magnesium methyl iodide containing 6 grams of magnesium. After remaining overnight, the product was decomposed by water and distilled in steam, the distillate was extracted with ether, the ethereal solution evaporated, and, in order to remove possible traces of unchanged ester, the oily residue was mixed with a solution of potassium hydroxide (3 grams) in methyl alcohol, and allowed to remain for twenty-four hours. After diluting with water, the pleasant-smelling oil was extracted with ether, the ethereal solution thoroughly washed, dried, and evaporated, and the *d*- Δ^6 -*m*-menthenol(8) distilled, when the whole quantity passed over at $106-107^\circ/20$ mm., and, as far as could be observed in the apparatus at our disposal, appeared to have no rotation (compare P., 1910, **26**, 97). A second sample was subsequently prepared and sent to Prof. Pope, who was good enough to examine it in his more accurate instrument, and found that it was laevorotatory, although only to a slight extent. The results of his measurements are as follows:

3.3354 grams, made up to 20.05 c.c. with pure ether, gave the following values in a 2-dcm. tube at 19.5° :

$\alpha -1.155^\circ$ for mercury green, whence $[\alpha]_{gr} -3.46^\circ$.

$\alpha -0.960^\circ$ for mercury yellow, whence $[\alpha]_{ye} -2.88^\circ$.

$\alpha -0.910^\circ$ for sodium yellow, whence $[\alpha]_D -2.73^\circ$.

The purity of the sample was tested by an analysis which gave the following results:

0.1451 gave 0.4140 CO_2 and 0.1551 H_2O . C=77.8; H=11.9.

$\text{C}_{10}\text{H}_{18}\text{O}$ requires C=77.9; H=11.9 per cent.

When this *d*- Δ^6 -*m*-menthenol(8) was left in contact with concentrated hydrochloric acid, crystallisation soon commenced, and, after remaining in the ice-chest for two days, the crystalline mass was transferred to porous porcelain and left over sulphuric acid until quite dry. The colourless residue then melted at $65-68^\circ$,

and, after once crystallising from methyl alcohol, from which it separated in brilliant leaflets, it melted sharply at 72° , had $\alpha_D + 22.5^{\circ}$, and consisted of pure *d*-sylvestrene dihydrochloride, $C_{10}H_{16} \cdot 2HCl$. The identity was established by analysis (Found, $Cl = 33.9$. $C_{10}H_{18}Cl_2$ requires $Cl = 34.0$ per cent.), and by the fact that, when mixed with a specimen of *d*-sylvestrene dihydrochloride from Swedish oil of turpentine, there was no alteration in melting point. In order to complete the synthesis of *d*-sylvestrene, the pure hydrochloride (7.5 grams) was decomposed by diethylaniline, the terpene distilled in steam, and, after extraction with ether, twice distilled over solid potassium hydroxide, when almost the whole quantity passed over at 175 — 178° , and had $\alpha_D + 67.5^{\circ}$, $d_{18} 0.8485$, and $n_D 1.4752$, whence $M = 45.25$ (calculated for $C_{10}H_{16} \equiv 45.24$). These values agree almost exactly with those observed by Wallach (*Annalen*, 1888, **245**, 198) in the case of a specimen of *d*-sylvestrene which he had obtained by distilling pure sylvestrene dihydrochloride from Swedish oil of turpentine with aniline, and which distilled at 175 — 176° and had $\alpha_D + 66.32^{\circ}$ and $n_D 1.4757$. There can thus be no doubt that the synthetical terpene, obtained as described above, is identical with the *d*-sylvestrene of Swedish oil of turpentine.

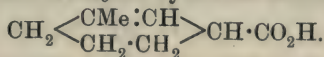
Synthesis of l-Sylvestrene.—In order to carry out this synthesis, *l*-1-methyl- Δ^6 -cyclohexene-3-carboxylic acid (11 grams of $\alpha_D - 98.6^{\circ}$; compare p. 2233) was converted into the methyl ester by treatment with methyl alcohol and sulphuric acid, and this, after isolation in the usual manner and without distillation, was mixed with an ethereal solution of magnesium methyl iodide containing 6 grams of magnesium.

The product was isolated in the manner already described in the case of the *d*-ester, and yielded 10 grams of *l*- Δ^6 -*m*-menthenol(8), which distilled at 106 — $108^{\circ}/21$ mm., and had a slight dextro-rotation of about $\alpha_D + 1^{\circ}$. In contact with concentrated hydrochloric acid, this menthenol was rapidly converted into a crystalline mass, which separated from methyl alcohol in glistening leaflets, melted at 70 — 72° , and had $\alpha_D - 21.8^{\circ}$. This *l*-sylvestrene dihydrochloride was decomposed by diethylaniline in the usual manner, and yielded *l*-sylvestrene, and, when this was twice carefully fractionated, the portion distilling at 176 — 178° had $\alpha_D - 68.2^{\circ}$, $d_{19} 0.848$, and $n_D 1.4761$, whence $M = 45.24$, whereas the value calculated for $C_{10}H_{16} \equiv$ is $M = 45.24$.

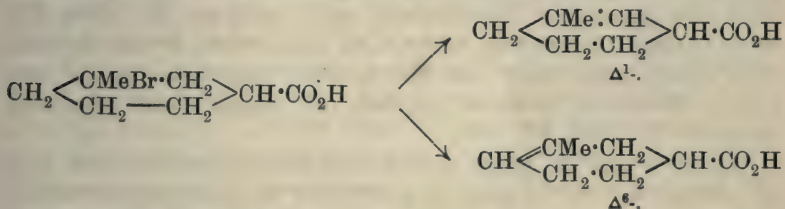
The final experiment was to mix equal quantities (0.5 gram) of *d*- and *l*-sylvestrene dihydrochlorides, and to recrystallise the product from a small quantity of methyl alcohol, when a considerable crop of crystals was obtained which melted sharply at

52° and consisted of *carvestrene dihydrochloride* (*dl*-sylvestrene dihydrochloride).

Resolution of dl-1-Methyl- Δ^1 -cyclohexene-3-carboxylic Acid,



It is stated in the introduction that the acid employed in these experiments and obtained by the elimination of hydrogen bromide from 1-bromo-1-methylcyclohexan-3-carboxylic acid, is a mixture of *dl*-1-methyl- Δ^1 - and *dl*-1-methyl- Δ^6 -cyclohexenecarboxylic acids:



and that this fact made the resolution and separation of the active constituents of the *dl*- Δ^1 -acid a very difficult and laborious process, which necessitated the use of a large quantity (295 grams) of the mixed acids. The process can only be indicated by the following examples: The mixed acids (in quantities of 70 grams) were dissolved in a slight excess of *N*/10-sodium hydroxide (510 c.c.), heated nearly to boiling, and then a hot aqueous solution of *l*-menthylamine hydrochloride (100 grams) was poured in with constant stirring. The oily layer which separated remained syrupy for several days, but, when vigorously stirred and left in the ice-chest, it gradually crystallised.

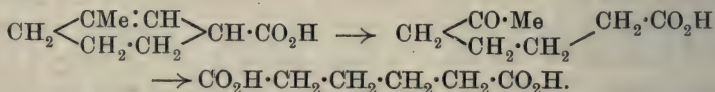
After fourteen days the aqueous layer was decanted, and yielded, on acidifying, nearly inactive acid (9 grams); the buttery menthylamine salt was left in contact with porous porcelain until quite dry, and the residue rubbed to a stiff paste with methyl ethyl ketone and again transferred to porous porcelain. The salt, which weighed 94 grams, was then twice recrystallised from methyl ethyl ketone, when it had $\alpha_D - 34.5^\circ$ and yielded an acid of rotation $\alpha_D - 16.3^\circ$. The plates containing the more soluble *l*-menthylamine salt were extracted with ether in a Soxhlet apparatus, the acid recovered, distilled, and treated again in the same manner, except that only 75 per cent. of the required amount of *l*-menthylamine was employed, and, by systematically continuing this process, 78 grams of acid, which had $\alpha_D - 16.5^\circ$, were separated from the 295 grams of the original mixture of *dl*-acids.

When this was repeatedly treated with *l*-menthylamine, an acid (22 grams) was gradually collected, which had $\alpha_D - 49.7^\circ$, and it

was found that this consisted of approximately pure *l*-1-methyl- Δ^1 -cyclohexene-3-carboxylic acid.

In order to demonstrate this, the unsaturated acid (5 grams) was dissolved in sodium carbonate and treated with ozone until absorption no longer took place; the product was then oxidised with permanganate at 0° until the colour persisted for two minutes. After acidifying, saturating with ammonium sulphate, and repeatedly extracting with ether on the machine, a syrup was obtained, which yielded bromoform when it was treated with sodium hypobromite, and evidently consisted of impure hexan- ϵ -one- α -carboxylic acid (acetylvaleric acid; compare T., 1890, 57, 230), $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, since, when it was digested with dilute nitric acid and the product evaporated to dryness under diminished pressure, crystals of adipic acid separated (compare T., 1907, 91, 497).

The formation of adipic acid proves that the unsaturated acid of rotation $\alpha_D - 49.7^\circ$ must be 1-methyl- Δ^1 -cyclohexene-3-carboxylic acid:



d-1-Methyl- Δ^6 -cyclohexene-3-carboxylic Acid.—After the mixture of *dl*-1-methyl- Δ^1 - and *dl*-1-methyl- Δ^6 -cyclohexene-3-carboxylic acids had been exhaustively treated with *l*-menthylamine in the manner just described, the acid was recovered from the mother liquors, distilled, and then converted into the brucine salt by the process described under method II on p. 2232. The resulting syrupy mixture of brucine salts was mixed with a little water and vigorously stirred from time to time, when, after some weeks, it deposited a considerable quantity of crystals, which were collected, several times recrystallised from water, and the acid recovered. This acid after distillation had $\alpha_D + 90.8^\circ$, and, although not optically pure (the rotation should have been $\alpha_D + 108^\circ$, compare p. 2232), this was proved to consist mainly of *d*-1-methyl- Δ^6 -cyclohexene-3-carboxylic acid, since, when converted into the methyl ester and this added to an ethereal solution of magnesium methyl iodide, it yielded *d*- Δ^6 -*m*-menthenol(8), which was almost inactive, and was converted into *d*-sylvestrene dihydrochloride (m. p. 72° ; $\alpha_D + 22.1^\circ$) by contact with concentrated hydrochloric acid.

This was indeed the first specimen of *d*- Δ^6 -*m*-menthenol(8) which was obtained, and which served for the first synthesis of *d*-sylvestrene, a preliminary description of which appeared in 1910 (P., 26, 97). The mother liquors of the brucine salt of the *d*- Δ^6 -acid must have contained *d*-1-methyl- Δ^1 -cyclohexene-3-carboxylic acid and

l-1-methyl- Δ^6 -cyclohexene-3-carboxylic acid, but no attempt was made to isolate these active constituents.

Conversion of l-1-Methyl- Δ^1 -cyclohexene-3-carboxylic Acid into *l*- Δ^1 -*m*-Menthenol(8) and *l*-Sylvestrene.

In this series of experiments, *l*-1-methyl- Δ^1 -cyclohexene-3-carboxylic acid of $\alpha_D -49.7^\circ$ (12 grams) was dissolved in 10 per cent. methyl-alcoholic sulphuric acid (100 c.c.), and, after two days, the methyl ester was isolated in the usual manner and distilled, when it passed over at $144-147^\circ/100$ mm. This ester was gradually added to an ethereal solution of magnesium methyl iodide (containing 6 grams of magnesium), and, after remaining overnight, the product was decomposed by water and distilled in steam. The distillate was extracted with ether, the ethereal solution evaporated, and the residue left in contact with alcoholic potassium hydroxide (KOH=3 grams) for twenty-four hours; water was then added, and the menthenol again extracted and distilled:

0.1318 gave 0.3771 CO_2 and 0.1402 H_2O . $\text{C}=77.8$; $\text{H}=11.8$.

$\text{C}_{10}\text{H}_{18}\text{O}$ requires $\text{C}=77.9$; $\text{H}=11.7$ per cent.

The *l*- Δ^1 -*m*-menthenol(8) thus obtained distilled at $106-108^\circ/20$ mm., and had $\alpha_D -45.9^\circ$, but this rotation, for reasons given on p. 2229, is probably somewhat lower than the true value. This menthenol gradually combines with hydrogen chloride, but not so readily as Δ^6 -*m*-menthenol(8) does, and, in contact with porous porcelain, the semi-solid product left a colourless, crystalline residue, which, after once crystallising from methyl alcohol, melted at 72° , had $\alpha_D -22.1^\circ$, and consisted of *l*-sylvestrene dihydrochloride, and when this was decomposed by diethylaniline it yielded a specimen of *l*-sylvestrene, which distilled at $175-178^\circ$ and had $\alpha_D -66.5^\circ$.

The authors are greatly indebted to repeated grants from the Research Fund of the Royal Society, which largely covered the heavy expense involved in this investigation.

THE UNIVERSITIES OF ST. ANDREWS, OXFORD AND MANCHESTER.

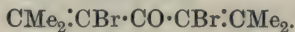
CCXXXIII.—*Some Derivatives of Phorone. Part I.*

By FRANCIS FRANCIS and FRANCIS GEORGE WILLSON.

THE great ease with which nitrosotriacetoneamine is catalytically decomposed into phorone, nitrogen, and water has been previously described (T., 1912, **101**, 2358), and the reaction has been utilised as a method for the determination of the concentration of hydroxyl ions (this vol., p. 1722).

There can be but little doubt that the formula used at present to represent the structure of phorone is correct, and that consequently this material affords an interesting basis for the study of chemical relations existing in a compound containing two adjacent pairs of conjugated double bonds—the so-called “cross-conjugated system.” We desired to commence this study by the investigation of some simple derivative of phorone, in which the magnitude of the residual affinities should be altered.

As phorone tetrabromide was found to be readily converted into a dibromo-derivative, we determined to investigate this first, since its method of preparation pointed to the conclusion that it was a dibromophorone of the constitution

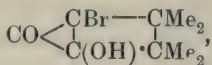


The replacement of two hydrogen atoms in phorone by bromine, however, results in the formation of a substance the properties of which differ more, from those of the parent material, than might have been expected.

The molecular refractivity of this dibromo-derivative showed an exaltation of 1·1, whereas phorone gives the abnormally high value of 3·0; further, the substance could not be directly brominated, did not combine with hydrogen bromide, and was curiously resistant towards oxidising agents.

The most characteristic reaction of this dibromo-derivative is the ease with which it is converted, by concentrated sulphuric acid, into a crystalline material of the molecular formula of a bromo-hydroxyphorone.

A study of the oxidation and reduction products of this derivative led us to formulate it as 1-bromo-2:2:3:3-tetramethylbicyclo-[0, 1, 2]pentan-4-ol-5-one:

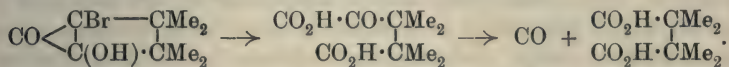


although the peculiar action of bromine on it cannot be said

to receive a very satisfactory explanation from such a conception of its constitution.

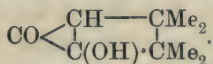
When this *bicyclopentanone* derivative is oxidised with alkaline permanganate it gives an excellent yield of a dibasic acid, $C_9H_{14}O_5$, and when this acid is warmed with concentrated sulphuric acid to 70–80° carbon monoxide is eliminated, and a quantitative yield of tetramethylsuccinic acid is obtained. The latter can also be obtained directly from the *bicyclopentanone* by oxidation with chromic and sulphuric acids.

These changes may be represented as follows:



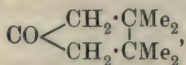
There can be little doubt that the oxidation of a derivative containing a five-membered ring had been carried out.

When the *bicyclopentanone* derivative is reduced with zinc dust and glacial acetic acid, the yield of reduction product obtained is very unsatisfactory; but it becomes quantitative if the acetyl derivative is employed. The reduced acetyl derivative which is formed is a liquid possessing a terpene-like odour, readily saponified by alkali, and the free hydroxyl derivative is a crystalline material which so closely resembles the parent substance in all its properties that we assign to it a similar constitution, namely, 2:2:3:3-tetramethylbicyclo[0, 1, 2]pentan-4-ol-5-one,



When the latter derivative, or the original *bicyclopentanone*, is reduced in alkaline solution by sodium amalgam, a substance of the formula $C_9H_{16}O$ results. This forms a semicarbazone, condenses with difficulty with aldehydes, and in appearance, odour, taste, and volatility shows a striking resemblance to camphor.

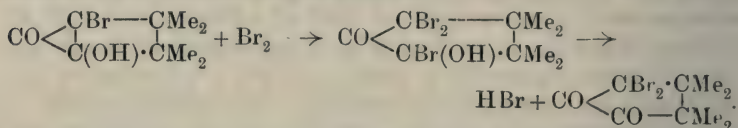
There is but little doubt that it is 1:1:2:2-tetramethylcyclopentan-4-one,



and we consider that the difficulty experienced in obtaining condensation products with aldehydes may be ascribed to the accumulation of methyl groups in the molecule.

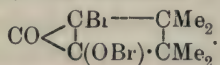
The action of bromine on the original *bicyclopentanone* derivative results in the formation of a red, crystalline dibromo-derivative, $C_9H_{12}O_2Br_2$. It was found that 1-bromo-2:2:3:3-tetramethylbicyclo[0, 1, 2]pentan-4-ol-5-one is not completely brominated in acetic acid solution unless one molecular proportion of

bromine was used for the purpose; this fact and the red colour of the derivative, suggesting an *o*-diketone structure, led us to formulate the bromination as follows:



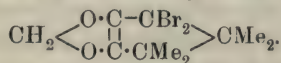
This explanation is based on K. Meyer's investigations of the action of bromine on substances of the nature of ethyl acetoacetate (*Annalen*, 1911, **380**, 212), and is supported by the fact that it was not found possible to brominate, in acetic acid solution, either the methyl or acetyl derivatives of 1-bromo-2:2:3:3-tetramethylbicyclo[0, 1, 2]pentan-4-ol-5-one, clearly indicating that the hydrogen of the hydroxyl group played a part in the reaction.

The dibromo-derivative is characterised by the great ease with which it is reconverted into 1-bromo-2:2:3:3-tetramethylbicyclo[0, 1, 2]pentan-4-ol-5-one, and this decomposition on the basis of the constitution we have assigned to the former, namely, 5:5-dibromo-1:1:2:2-tetramethylcyclopentan-3:4-dione, appears to indicate that under certain conditions it can functionate in the tautomeric form expressed by the formula



Although under one set of conditions one bromine atom is readily eliminated, yet such reagents as alkali hydroxides, or sodium acetate in alcoholic solution, yield bromine-free derivatives. The diacetate which results from the latter decomposition has been analysed, but the product from the action of alkalis is a syrup which, so far, we have been unable to investigate.

The only derivative of the red dibromo-derivative still containing two bromine atoms, which it has been found possible to isolate, is one resulting from the action of diazomethane on its ethereal solution. This is a colourless, crystalline material, differing only from the parent bromide by CH_2 , and to which, based on our previous conceptions, we provisionally assign the constitution:



The investigation is being continued, and it is hoped that further light will be thrown on these interesting substances.

EXPERIMENTAL.

Phorone tetrabromide has been described by Claisen, and is readily prepared by the action of bromine on phorone in carbon

disulphide or carbon tetrachloride solution. If the bromination is carried out in alcoholic solution an oil is obtained with properties altogether different from those of the tetrabromide, and it is proposed to investigate this substance at a later date.

Dibromophorone.

When the tetrabromide is dissolved in a little more than its own weight of cold pyridine, and the solution kept for twenty-four hours, the above is formed, and can be isolated by the addition of a large excess of water, when it is precipitated as an oil, which is obtained in quantitative yield and in a high state of purity by washing with water and then 30 per cent. sulphuric acid. The latter process must be thoroughly carried out, since the dibromo-derivative retains traces of pyridine with great tenacity, but when freed from this base the oil usually crystallises at once.

The compound crystallises in large, transparent, slightly yellow prisms, and melts at 32° . It may be distilled under greatly diminished pressure with but slight decomposition, it is extremely soluble in the usual organic solvents, possesses a faint odour resembling that of pine, and on exposure to the air rapidly becomes green:

0.4111 gave 0.5289 AgBr. Br=54.7.

$C_9H_{12}OBr_2$ requires Br=54.2 per cent.

The dibromo-derivative has a density of 1.552 at 37.4° , and the refractive index at this temperature for the *D*-line is 1.53941, and for the *C*-line 1.53460; this gives a molecular refractivity of 59.77 and 59.37 respectively, and an exaltation of 1.09 and 1.12, based on the formula we have assigned to this substance. The magnitude of this exaltation is what might have been expected in such a cross-conjugated system, but is very much less than that of phorone itself, which, according to Brühl, is 3.05.

The dibromo-derivative is either unacted on by reducing agents or else a very small yield of phorone is obtained. Oxidising agents have no action on it. When dissolved in carbon disulphide and treated with excess of bromine, it can be recovered unchanged; it is also unacted on when dissolved in a concentrated acetic acid solution of hydrogen bromide and allowed to remain for two weeks.

1-Bromo-2:2:3:3-tetramethylbicyclo[0, 1, 2]pentan-4-ol-5-one.

The best method for the preparation of this substance consists in acting on dibromophorone in the cold with about three molecular proportions of concentrated sulphuric acid and allowing the mixture to remain for twenty-four hours. Bromine and hydrogen bromide

are evolved, and the product is isolated by pouring the solution on to crushed ice.

By using not more than 50 grams of the dibromo-derivative at one operation, a yield of 82 per cent. of the *bicyclopentanone* derivative can be obtained.

The substance is best crystallised from dilute alcohol, from which solvent it separates in well-formed, colourless needles, melting at 116° . It is soluble in hot water, slightly volatile with steam, and its behaviour in this boiling solvent recalls that of benzoic acid. It is extremely stable towards concentrated sulphuric acid, and its solution in this medium may be heated to a temperature of 200° without showing any signs of decomposition:

0.1554 gave 0.2640 CO_2 and 0.0796 H_2O . $\text{C}=46.33$; $\text{H}=5.69$.

0.5768 „ 0.4636 AgBr . $\text{Br}=34.14$.

$\text{C}_9\text{H}_{13}\text{O}_2\text{Br}$ requires $\text{C}=46.34$; $\text{H}=5.58$; $\text{Br}=34.34$ per cent.

A determination of the molecular weight by the ebullioscopic method, using acetone as solvent, gave the following result:

1.0221 in 19.8 gave Δt 0.360 . $\text{M.W.}=244$.

$\text{C}_9\text{H}_{13}\text{O}_2\text{Br}$ requires $\text{M.W.}=233$.

This compound possesses well-marked acidic properties, a hot aqueous solution reddens litmus paper, it is easily soluble in solutions of the alkalis and in alkaline carbonates, and the sodium salt separates from concentrated solutions in characteristic silky needles.

We were unable to obtain either an oxime or semicarbazide, probably due to the presence of substituents on either side of the carbonyl group.

The presence of one hydroxyl group was confirmed by the formation of the following derivatives:

The *acetyl* derivative, prepared by boiling the *bicyclopentanone* for one hour with excess of acetic anhydride, recrystallises from dilute acetic acid in long, colourless needles, melting at 74° :

0.1562 gave 0.2782 CO_2 and 0.0807 H_2O . $\text{C}=48.57$; $\text{H}=5.74$.

0.605 „ 0.4172 AgBr . $\text{Br}=29.34$.

$\text{C}_{11}\text{H}_{15}\text{O}_3\text{Br}$ requires $\text{C}=48.01$; $\text{H}=5.45$; $\text{Br}=29.09$ per cent.

The *benzoyl* derivative was obtained in the usual way, using pyridine as solvent. After crystallisation from dilute alcohol it melts at 92° :

0.184 gave 0.3825 CO_2 and 0.0892 H_2O . $\text{C}=56.7$; $\text{H}=5.38$.

$\text{C}_{19}\text{H}_{17}\text{O}_3\text{Br}$ requires $\text{C}=56.98$; $\text{H}=5.04$ per cent.

The *carbomethoxy*-derivative, after crystallisation from dilute alcohol and ether, melts at $75-77^{\circ}$:

0.205 gave 0.3396 CO₂ and 0.0954 H₂O. C=45.18; H=5.17.

C₁₁H₁₅O₄Br requires C=45.36; H=5.15 per cent.

Oxidation of 1-Bromo-2:2:3:3-tetramethylbicyclo[0, 1, 2]pentan-4-ol-5-one.

Ten grams of this derivative were dissolved in an excess of potassium hydroxide and oxidised with a solution of 15 grams of potassium permanganate, care being taken not to allow the temperature to rise. On acidification and repeated extraction with ether, 8 grams of an oil were obtained, which set to a very hard, crystalline mass on keeping. After solidification it could be recrystallised from toluene, and melted at 139°:

0.2416 gave 0.4732 CO₂ and 0.1492 H₂O. C=53.42; H=6.86.

C₉H₁₄O₅ requires C=53.46; H=6.93 per cent.

A determination of the molecular weight by the ebullioscopic method, using acetone as solvent, gave the following result:

0.1612 in 12.70 gave Δt 0.120°. M.W.=180.

C₉H₁₄O₅ requires M.W.=202.

This substance was readily soluble in water, gave a strongly acid solution, and was shown to be dibasic by an analysis of its *silver* salt:

0.4410 gave 0.2325 Ag. Ag=52.60.

C₉H₁₂O₅Ag₂ requires Ag=51.93 per cent.

In order to determine the number of hydroxyl groups, a specimen of the pure acid was treated with excess of diazomethane in ethereal solution. The resulting oil was fractionated in a vacuum, and the main bulk of the methyl derivative boiled at 160°/50 mm. On keeping for a long period this oil set to a crystalline mass, which melted at 93—97° on recrystallisation from benzene and light petroleum. The analysis showed that a dimethyl derivative only had been formed, and hence that there were only two hydroxyl groups present:

0.2133 gave 0.4436 CO₂ and 0.1479 H₂O. C=56.71; H=7.71.

C₁₁H₁₈O₅ requires C=57.39; H=7.82 per cent.

Since this acid can be quantitatively converted into dimethylsuccinic acid, there can be no doubt that it is α -keto- $\beta\gamma$ -tetramethylglutaric acid, CO₂H·CO·CMe₂·CMe₂·CO₂H.

On reduction with sodium amalgam in alkaline solution this acid passes quantitatively into the lactone of α -hydroxy- $\beta\gamma$ -tetramethylglutaric acid, an oil which slowly solidifies to a crystalline mass; this may then be purified by recrystallisation from benzene and light petroleum, and melts at 68°:

0.2168 gave 0.4578 CO_2 and 0.1503 H_2O . $\text{C}=57.58$; $\text{H}=7.65$.

$\text{C}_9\text{H}_{14}\text{O}_4$ requires $\text{C}=58.06$; $\text{H}=7.52$.

An analysis of the *silver* salt of this lactonic acid showed that it was monobasic:

0.4880 gave 0.1798 Ag. $\text{Ag}=36.85$.

$\text{C}_9\text{H}_{13}\text{O}_4\text{Ag}$ requires $\text{Ag}=36.85$ per cent.

When α -keto- β -tetramethylglutaric acid was warmed to 80° with concentrated sulphuric acid, carbon monoxide was evolved, and a quantitative yield of tetramethylsuccinic acid obtained. This acid (m. p. 180 — 190°) gave correct data on analysis, and was characterised by conversion into its anhydride, which melted at 147° , and also gave correct analytical data.

Tetramethylsuccinic acid was also obtained by the direct oxidation of the *bicyclopentanone* derivative with chromic acid.

Reduction of 1-Bromo-2:2:3:3-tetramethylbicyclo[0, 1, 2]pentan-4-ol-5-one.

This derivative gives only a very poor yield of reduction product when treated with zinc dust and glacial acetic acid, but when the acetyl derivative is used an excellent yield of the acetyl derivative of 2:2:3:3-tetramethylbicyclo[0, 1, 2]pentan-4-ol-5-one is obtained. This derivative is an oil, which is easily saponified by warming with dilute alkalis; when this solution is acidified and extracted with ether, the parent substance is obtained, which fuses at 86° on recrystallisation from boiling water.

In appearance and solubility it closely resembles the bromo-derivative; it also possesses a very similar, but somewhat more pungent, odour, and shows the same acid properties:

0.2190 gave 0.5618 CO_2 and 0.1788 H_2O . $\text{C}=69.96$; $\text{H}=9.07$.

$\text{C}_9\text{H}_{14}\text{O}_2$ requires $\text{C}=70.13$; $\text{H}=9.09$ per cent.

The *benzoyl* derivative, prepared by the ordinary method, melts at 69° on crystallisation from dilute alcohol:

0.2324 gave 0.6330 CO_2 and 0.1470 H_2O . $\text{C}=74.29$; $\text{H}=7.03$.

$\text{C}_{16}\text{H}_{18}\text{O}_3$ requires $\text{C}=74.42$; $\text{H}=6.98$ per cent.

When 1-bromo-2:2:3:3-tetramethylbicyclo[0, 1, 2]pentan-4-ol-5-one is reduced in alkaline solution by 2 per cent. sodium amalgam, a strong odour of camphor soon becomes apparent, and the reduction product separates in flakes which can be extracted with ether.

The derivative is purified with difficulty by crystallisation from dilute alcohol and ether; it melts at 130° , and sublimes so readily that it cannot be dried in a vacuum. The same substance can also

be obtained by the reduction, under similar conditions, of 2:2:3:3-tetramethylbicyclo[0, 1, 2]pentan-4-ol-5-one.

The material is only sparingly soluble in water, but dissolves in the ordinary organic solvents, and has an appearance, odour, and taste curiously similar to that of camphor, and, like that substance, feels the same when pressed or cut with a spatula:

0.2086 gave 0.5884 CO₂ and 0.2152 H₂O. C=76.91; H=11.47.

C₉H₁₆O requires C=77.14; H=11.43 per cent.

A determination of the molecular weight by the ebullioscopic method, using acetone as solvent, gave the following result:

1.4367 in 16.36 gave Δt 1.008. M.W.=148.

C₉H₁₆O requires M.W.=140.

The *semicarbazone* obtained in the usual manner melted at 223° on recrystallisation from dilute alcohol:

0.144 gave 26.6 c.c. N₂ at 13.5° and 759.7. N=21.78.

C₁₀H₁₉ON₃ requires N=21.32 per cent.

There can be but little doubt that the substance described is 1:1:2:2-tetramethylcyclopentan-4-one, but, unlike cyclic ketones of this class, it does not condense at all readily with aldehydes. Both with benzaldehyde and with *o*- and *m*-nitrobenzaldehyde, under the influence of sodium ethoxide, small quantities of yellow condensation products were obtained, but analysis showed that these were mixtures of mono- and di-benzylidene derivatives, which, with the small amount at our command, we were unable to separate.

When 1:1:2:2-tetramethylcyclopentan-4-one is oxidised with hydrogen peroxide in alkaline solution an acid results, which may be crystallised from a small quantity of water, or from benzene, and melts at 131°. The analysis indicated that this substance was $\alpha\beta$ -tetramethylglutaric acid, CO₂H·CH₂·CMe₂·CMe₂·CO₂H:

0.2272 gave 0.4794 CO₂ and 0.1662 H₂O. C=57.53; H=8.14.

C₉H₁₆O₄ requires C=57.45; H=8.51 per cent.

Action of Bromine on 1-Bromo-2:2:3:3-tetramethylbicyclo[0, 1, 2]pentan-4-ol-5-one.

Bromine does not act on the above compound in carbon disulphide solution, but one molecular proportion gives a quantitative yield of a dibromo-derivative when the operation is carried out in glacial acetic acid. The compound is insoluble in water, and may be purified by rapid crystallisation from alcohol. It is an orange, crystalline substance, melting at 182°.

From the analysis and molecular-weight determination we consider that this substance is 5:5-dibromo-1:1:2:2-tetramethylcyclopentane-3:4-dione:

0.1457 gave 0.185 CO_2 and 0.0507 H_2O . $\text{C}=34.63$; $\text{H}=3.87$.

0.4587 „ 0.5602 AgBr . $\text{Br}=51.96$.

$\text{C}_9\text{H}_{12}\text{O}_2\text{Br}_2$ requires $\text{C}=34.61$; $\text{H}=3.85$; $\text{Br}=51.28$ per cent.

The molecular weight was determined by the ebullioscopic method, using acetone as solvent:

0.3466 in 14.79 gave Δt 0.178. $\text{M.W.}=288$.

$\text{C}_9\text{H}_{12}\text{O}_2\text{Br}_2$ requires $\text{M.W.}=312$.

Neither the acetyl nor the methyl derivatives of 1-bromo-2 : 2 : 3 : 3 - tetramethylbicyclo[0, 1, 2]pentan-4-ol-5-one could be brominated in acetic acid solution.

By far the most characteristic reaction of this dibromo-derivative was the ease with which it was reconverted into the substance from which it was obtained; a decomposition brought about quantitatively by concentrated sulphuric acid or by reduction with zinc dust and glacial acetic acid, and partly by boiling with water, alcohol, or acetone.

This decomposition clearly points to the fact that one bromine atom is situated differently from the other.

Although under the above conditions one bromine atom alone is eliminated, yet when the dibromo-derivative is acted on by alkalis in aqueous suspension a substance is obtained free from bromine. The yield of the latter, however, is small, and the substance is a syrup, which we have been unable to obtain in quantity in the crystalline form. A small specimen recrystallised from benzene in light petroleum melted at 68° .

When the dibromo-derivative is boiled with an excess of alcoholic sodium acetate a crystalline *diacetate* is obtained, which melts at $100\text{--}102^\circ$ on recrystallisation from dilute acetic acid:

0.1468 gave 0.3118 CO_2 and 0.0898 H_2O . $\text{C}=57.91$; $\text{H}=6.79$.

$\text{C}_{13}\text{H}_{18}\text{O}_6$ requires $\text{C}=57.77$; $\text{H}=6.66$ per cent.

This diacetate is readily decomposed by dilute alkalis, and the resulting substance is a syrup which we believe to be identical with that mentioned in the last paragraph. A small quantity of this was also obtained in the crystalline form and melted at 67° , and this melting point remained unchanged when the substance was mixed with some of the product obtained by the action of alkalis on the dibromo-derivative.

The only derivative of the latter compound that we have been able to obtain, which still contains two bromine atoms, is that which results when its ethereal solution is treated with diazomethane. This derivative, which is colourless, crystallises indifferently, and the crystals feel sticky, although showing a definite melting point of 190° after repeated recrystallisations from dilute acetic acid:

0.2274 gave 0.3066 CO_2 and 0.0904 H_2O . $\text{C}=36.77$; $\text{H}=4.42$.
 0.4578 „ 0.5299 AgBr . $\text{Br}=49.25$.
 $\text{C}_{10}\text{H}_{12}\text{O}_2\text{Br}_2$ requires $\text{C}=36.81$; $\text{H}=4.29$; $\text{Br}=49.08$ per cent.

Our thanks are due to Mr. D. A. Clibbens for the great assistance he gave one of us in the preliminary investigation of the *bicyclopentanone* and its dibromo-derivative.

THE CHEMICAL DEPARTMENT,
 UNIVERSITY OF BRISTOL.

CCXXXIV.—*Amalgams Containing Silver and Tin.*

By WILLIAM ARTHUR KNIGHT and REGINALD ARTHUR JOYNER.

THE present investigation is a continuation of work done in this laboratory by one of us on the chemistry of the ternary system tin-silver-mercury (T., 1911, **99**, 195; also McBain and Joyner, *Dental Cosmos*, June, 1912). In that communication it was firmly established that freshly filed alloys of silver and tin require about twice as much mercury for amalgamation as filings which have been heated to 100° for half-an-hour, or which have been kept at room temperature for several months after filing. The latter kinds of filings are said to be "aged." In addition to a thorough investigation of this "ageing" of filings of silver-tin alloys, the communication mentioned above contained an account of work done on the chemistry of the binary systems silver-tin, silver-mercury, tin-mercury, whilst the ternary system silver-tin-mercury was studied at temperatures up to 63° .

The object of the present investigation was to check and confirm some of the previous conclusions with regard to ageing, and to study the ternary diagram at higher temperatures.

Throughout the present communication the composition of the alloys and amalgams is everywhere expressed in atomic percentages, but the percentages of tin and silver in the liquid amalgams as given in tables III—VI of the previous communication are percentages by weight.

PART I.

The Ageing of Filings of Alloys of Silver and Tin.

Although no satisfactory explanation of the mechanism of this process has been advanced, its existence was proved conclusively

by the results given in the previous communication. It has been suggested (H. B. Baker, *Ann. Reports*, 1911, **8**, 36) that the experiments described did not absolutely disprove the hypothesis that the ageing of a dental alloy may be due to a superficial film of oxide formed during the heating, especially since many metals oxidise very readily when they are ground in an agate mortar.

We desire to take this opportunity (compare Baker, *loc. cit.*, with Joyner, *loc. cit.*, p. 195) of stating categorically that it is an obvious *sine qua non* of work such as that described in this and the previous communication that all experiments on alloys, filings, or amalgams above room temperature are carried out in a reducing atmosphere of hydrogen or coal gas. This also applies to the preparation of the alloys when fusing their constituents together. Apart from the few particular experiments specially indicated, this condition has been observed throughout.

The following further experiments were therefore carried out by one of us, and fully confirm those previously published by the other:

(1) A quantity of the alloy Ag_3Sn was very slowly filed, the bar of alloy being cooled in running water every ten seconds. Some of this filed alloy was pulverised in an agate mortar, and was then weighed and shaken for two minutes with excess of mercury. The excess of mercury was squeezed out through chamois leather by the application of a 56 lb. weight (25 kilos.), as described in the previous communication (*loc. cit.*, p. 198). The amalgam remaining was then weighed. It was found that

$$\frac{\text{Wt. of mercury retained}}{\text{Wt. of alloy taken}} = \frac{6.081}{2.414},$$

$$= \frac{2.52}{1}.$$

These filings have therefore remained "unaged" in spite of having been ground fine in an agate mortar. This confirms the experiment previously published (Joyner, *loc. cit.*, p. 203), which Baker appears to have overlooked.

(2) A similar experiment was performed, but the filings of the alloy Ag_3Sn were "aged" before pulverisation by heating for half-an-hour at 100° in an atmosphere of coal-gas. It was found that

$$\frac{\text{Wt. of mercury retained}}{\text{Wt. of alloy taken}} = \frac{3.448}{3.212},$$

$$= \frac{1.07}{1}.$$

These filings are therefore still "aged." Hence pulverisation in an agate mortar does not age unaged alloy, nor does it unage aged alloy. This shows that the hypothesis that ageing may be due to

superficial oxidation is untenable. For, if such were the case, pulverisation would either remove the film of oxide exposing fresh surfaces of alloy on which mercury would readily react, thus unaging those filings, or, likewise contrary to fact, unaged filings would thereby become aged.

(3) Two lots of filings of the alloy Ag_3Sn were prepared similarly, and were heated in sealed tubes for half-an-hour at 100° . The tubes had been washed out four times with coal gas after introducing the filings, and finally one tube was filled with coal gas whilst the other was thoroughly exhausted by a Fleuss pump before they were sealed up. After heating, the contents of each tube were pulverised in the agate mortar, amalgamated, and the excess of mercury squeezed out as before. The results obtained were as follows:

(a) *Tube Filled with Coal Gas.*

$$\begin{aligned}\frac{\text{Wt. of mercury retained}}{\text{Wt. of alloy taken}} &= \frac{1.522}{1.806}, \\ &= \frac{0.84}{1}.\end{aligned}$$

(b) *Tube Exhausted.*

$$\begin{aligned}\frac{\text{Wt. of mercury retained}}{\text{Wt. of alloy taken}} &= \frac{1.877}{2.400}, \\ &= \frac{0.78}{1}.\end{aligned}$$

Hence both lots of filings were still aged.

(4) Efforts were again made to "age" a solid bar of alloy. The bar of Ag_3Sn was heated in a sealed tube filled with coal gas for five days at 115° . After filing, pulverising, and amalgamating as before, it was found that

$$\begin{aligned}\frac{\text{Wt. of mercury retained}}{\text{Wt. of alloy taken}} &= \frac{5.112}{2.068}, \\ &= \frac{2.47}{1}.\end{aligned}$$

On heating to 115° for a further four days, filings from the same bar gave

$$\frac{\text{Wt. of mercury retained}}{\text{Wt. of alloy taken}} = \frac{2.33}{1},$$

whilst after six days more at the same temperature

$$\frac{\text{Wt. of mercury retained}}{\text{Wt. of alloy taken}} = \frac{2.29}{1}.$$

The bar has therefore remained "unaged." It seems, therefore, no longer possible to ascribe ageing to any (uncatalysed) polymorphic change, since ageing does not take place in a bar of alloy

heated during several weeks, whereas it occurs with unfailing regularity in filings heated for half-an-hour.

(5) Ageing might be due to sorption of oxygen by the filings, but such oxygen cannot have any effect if magnesium is added to the alloy before filing. Hence, in order to test this hypothesis, the following experiment was carried out.

Part of a bar of the alloy Ag_3Sn was melted with about 1 per cent. of its weight of magnesium in an atmosphere of coal gas. After allowing the resulting alloy to solidify, it was re-melted with vigorous shaking, and again allowed to solidify. The alloy prepared in this way must have been thoroughly mixed. Filings of this alloy were amalgamated, and the excess of mercury squeezed out exactly as in previous experiments. The result gave:

$$\begin{array}{rcl} \text{Wt. of mercury retained} & = & 4.733 \\ \text{Wt. of alloy taken} & = & 2.143' \\ & = & 2.21 \\ & = & 1 \end{array}$$

A second quantity of these filings was "aged" before amalgamation, and it was found that

$$\begin{array}{rcl} \text{Wt. of mercury retained} & = & 2.977 \\ \text{Wt. of alloy taken} & = & 2.781' \\ & = & 1.07 \\ & = & 1 \end{array}$$

This experiment thus disproves the hypothesis that ageing is due to sorption of oxygen by the filings.

Although the mechanism of ageing is as yet quite unknown to us, it might be due to a polymorphic change, which, as it does not take place with sensible velocity until the bar of alloy is filed up, may possibly be enormously accelerated by the iron or products of iron introduced during the filing.*

PART II.

The Ternary System: Silver-Tin-Mercury.

In the previous communication it is stated that there are two groups of equilibria in this system corresponding with higher and lower temperatures respectively. Further investigation, however, has shown that, although this view is not quite strictly correct, it is true for all practical purposes. The evidence in favour of it was that the cooling curves of all amalgams of silver and tin show breaks at temperatures between 65° and 100° . This might have

* That a change does take place in the Ag_3Sn filings we have established by density determinations; these will be included in a later communication.

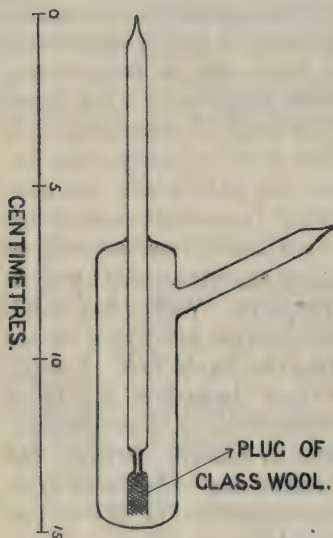
been interpreted as being due to the formation of a ternary compound at higher temperatures. These breaks may also be taken as indicating that the particular amalgam under consideration has crossed from a field of three phases (*E* in Fig. 1) to a field of two phases (*B* in Fig. 1), owing to the broadening out of this latter region as the temperature rises. It is shown in the sequel that the latter interpretation is correct, and that no ternary compound is formed.

Systems Containing Wholly or Partly Liquid Amalgams.

The study of the composition of the liquid amalgams in contact with one or more solids not only establishes by direct experiment the exact delimitations of the liquids which are so important a feature of this system, but derives special significance when interpreted in the light of the phase rule. This mode of attack, which is not usually available, enables us to deduce with certainty, from the position and shape of the liquid region, the nature and the composition of the solids capable of existing in contact with these liquids. The phase rule predicts that, in a ternary system such as the present, not more than two solids can simultaneously exist in contact with liquid at any given temperature. Where two solids are present the liquid will have a fixed composition lying at the intersection of two of the curves bounding the liquid field. Liquids situated along the smooth boundary curves themselves can be in contact with only one solid element or compound or solid solution; thus the number of solid phases present is known. Finally, the nature and composition of the solids present can be deduced from a knowledge of the initial percentage composition of the system and the composition of the resulting liquid.

This method has here been employed at the following temperatures: 63°, 90°, 166°, and 214°. Thus for each temperature we have obtained an equilibrium diagram showing the composition and extent of all saturated and unsaturated liquids (region denoted by the letter *A* in the diagrams), together with the delimitation of all the adjacent heterogeneous fields, leaving only a small portion of the diagram consisting of solids very rich in silver, but containing very little tin still to be investigated. For this the ordinary metallographic methods will be available. The result is to disprove the existence of any ternary compound of silver, tin, and mercury, but, on the other hand, to demonstrate the existence of a single series of solid solutions indistinguishable from "*Arbor Dianae*," Ag_3Hg_4 , at room temperature. At high temperatures this series of solid solutions lengthens out from this composition of Ag_3Hg_4 roughly in the direction of Ag_3Sn as the temperature is raised.

In order to determine the composition of the liquid phase at any temperature, weighed amounts of the three metals were introduced into the reaction tube, from which all air was removed by washing out the tube by means of coal gas after introducing the metals. The reaction tubes at the lower temperatures, where the vapour pressure of mercury is small, were not completely immersed in the thermostat. At the higher temperatures the tubes were sealed off and totally immersed, the drawn out portion being scratched so as to admit of breaking it within a rubber tube connected with hydrogen or coal gas while keeping it still in the thermostat.



REACTION TUBE.

These tubes for the higher temperatures were of the shape and approximately of the size shown. Scrupulous care must be taken to ensure that all the solid has really come into contact with all the liquid.

At 166° a heavy oil was employed as thermostat liquid. The particular oil used was obtained through Messrs. Baird and Tatlock from Price's Patent Candle Co., and gave off little odour even at 166° . At 214° the oil was replaced by the eutectic mixture of potassium and sodium nitrates (45.5 per cent. by weight of the latter), to which a quantity of lithium nitrate had been added sufficient to ensure its remaining liquid at about 205° , as the eutectic mixture of potassium and sodium nitrates solidifies at 218° .

No difficulty was experienced in maintaining the temperature of the melted nitrates constant to within 0.2° during any individual experiment, although the mercury regulator was simply a length of iron gas piping.

After the reaction tubes had remained in the thermostat for a sufficiently long time to ensure the attainment of equilibrium—this time varied from four days at the low temperatures to as many hours at the high temperatures—part of the liquid phase was removed and analysed in the same way as is described in the previous communication.

The tables which follow give:

(1) The gross composition of the mixtures with which the reaction tubes were charged.

(2) The composition of the liquid phase as determined by analysis.

(3) The letters by which the corresponding points on the diagram are designated.

The positions of the points representing the gross compositions are indicated thus \odot , whilst the points on the liquid curves are shown thus \times , corresponding points being represented everywhere by the same letter. All compositions are given in atomic percentages of the metals employed.

TABLE I.

Temp. $63\cdot10^{\circ}\pm0\cdot05$.

Gross composition.			Composition of liquid phase.			Point on diagram.
Ag.	Sn.	Hg.	Ag.	Sn.	Hg.	
35·0	2·0	63·0	0·21	1·82	98·0	<i>a</i>
35·0	2·75	62·25	0·36	4·04	95·6	<i>b</i>
35·0	3·5	61·5	0·06	4·16	95·77	<i>c</i>

The atomic percentage of silver in the liquid phase corresponding with the point *c* is too low owing to error in the analysis, but previous determinations (T., 1911, 99, 208) in the case of saturated amalgams render this of little importance.

From the results of table I combined with those given on p. 208 of the previous communication, it is possible to construct the cross-section of the thermal diagram at this temperature; thus when the results mentioned last are re-calculated in atomic percentages we have the following values:

Solubility of silver in mercury at $63^{\circ}=0\cdot191$ at. per cent.

Solubility of tin in mercury at $63^{\circ}=3\cdot884$ at. per cent.

The other results of this table represent amalgams saturated with respect to both silver and tin, and their liquid phases coincide with the intersection of the liquid curves at *c*.

The cross-section at 63° of the thermal diagram is given in Fig. 1.

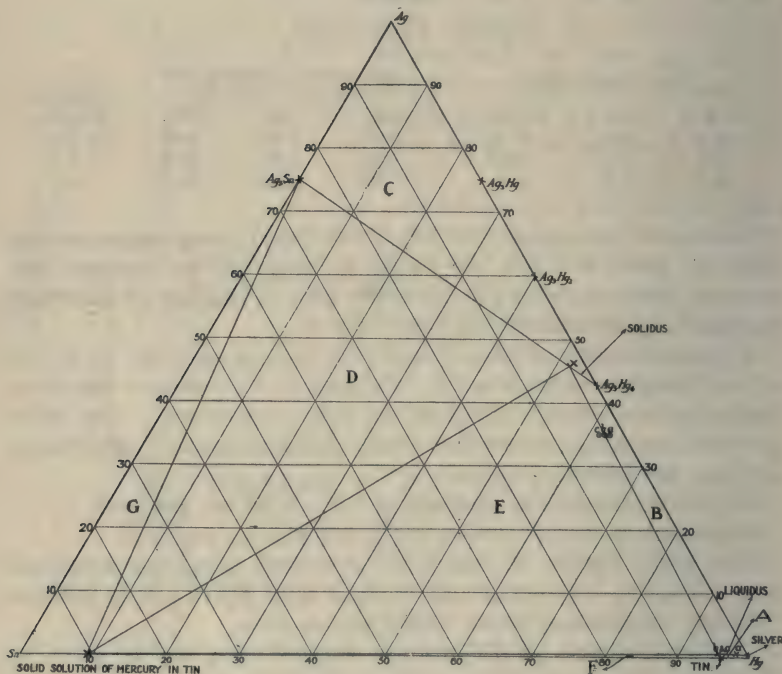
The explanation of this figure is as follows: The pure metals occupy the angular points of the equilateral triangle. On the side Ag-Sn is marked the position of the only compound which silver forms with tin, namely, Ag_3Sn , containing 75 atoms per cent. of silver. Now silver and mercury form three compounds, Ag_3Hg_4 , Ag_3Hg_2 , and Ag_3Hg , which are shown in their proper positions on the side Ag-Hg. Tin and mercury do not form a compound, but the solid crystallising out at any temperature consists of a solid solution of mercury in tin. At 63° this solid solution contains 9·5 atoms per cent. of mercury (K. Bornemann, "Die binären Metallegierungen," Teil II., Tafel 14). This point is marked on the

Sn-Hg side of the triangle. In addition there is shown the position of the saturated solution of silver in mercury at "Silver," and that of the saturated solution of tin in mercury at "Tin." On joining up the points as shown in the figure, it will be seen that at 63° :

(1) All points in the field *A* represent liquids. This field *A* is bounded by two continuous curves and by the Sn-Hg side of the triangle.

(2) All mixtures the compositions of which are represented by

FIG. 1.



points in the field *B* give a liquid represented by a point on the liquidus, together with a solid solution represented by a corresponding point on the solidus. It is a geometrical requirement that if a straight line is drawn from the point on the liquidus to the point representing the gross composition of the original mixture this straight line must pass through the point on the solidus representing the composition of the solid solution. That the solids in this heterogeneous field must be solid solutions is a requirement of the phase rule. For by the phase rule it follows that in a system consisting of three metals there can only be one solid phase

in regions where the liquid phase varies, and a series of solid solutions is the only way in which this single phase can be constituted, since the locus of the prolongations is a curve. Had the solid been a definite compound, all the prolongations would have passed through the one point representing its composition on the diagram. That there is good reason for considering the line drawn from Ag_3Hg_4 to X as approximately the solidus will be seen later.

(3) In all regions such as *G* a mixture of the three metals in the proportions represented by any point within the area considered gives the substances represented by the angular points of that region; thus any point within the area *G* gives the three substances Ag_3Sn , Sn, and saturated solution of mercury in tin. The proportions in which these substances are formed depends on the position of the point representing the gross composition of the original mixture.

The results of table I can be exhibited in a different way as follows: We can calculate for each point the number of atoms of silver and of tin associated with 100 atoms of mercury. The results of this calculation are as follows:

TABLE Ia.

Point on diagram.	No. of atoms of silver to 100 atoms of mercury.	No. of atoms of tin to 100 atoms of mercury.
"Silver"	0.19	—
<i>a</i>	0.21	1.86
<i>b</i>	0.38	4.23
<i>c</i>	(as <i>b</i> 0.38)	4.34
"Tin"	—	4.04

The number of atoms of silver thus obtained may be plotted as ordinates against the number of atoms of tin as abscissæ. Taken in conjunction with similar diagrams at higher temperatures (see below) consisting of two flat curves meeting at a point, it is clear that no definite compound between silver, tin, and mercury is formed.

TABLE II.

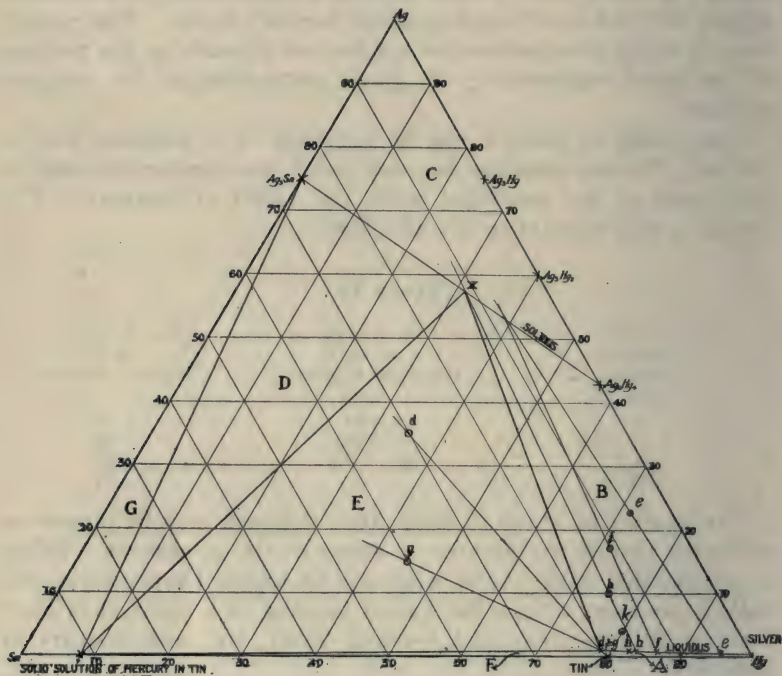
Temp. $90.0^\circ \pm 0.2$.

Gross composition.			Composition of liquid phase.			Point on diagram.
Ag.	Sn.	Hg.	Ag.	Sn.	Hg.	
35.0	Pure silver	35.0	0.33	—	99.67	"Silver"
22.8	30.0	71.5	1.00	20.6	78.4	<i>d</i>
17.1	5.7	71.5	0.53	4.2	95.3	<i>e</i>
15.0	11.4	71.5	0.80	12.9	86.3	<i>f</i>
15.0	40.0	45.0	0.96	20.5	78.5	<i>g</i>
10.0	15.0	75.0	0.88	15.7	83.4	<i>h</i>
4.0	16.0	80.0	0.92	16.6	82.4	<i>k</i>
	Pure tin		—	20.0	80.0	"Tin."

The last value is taken from the diagram in Bornemann's book previously referred to.

The results of table II are shown in Fig 2, where the different fields are represented by the same letters as in Fig. 1. We see that the liquid field *A* has increased considerably in length, and also that it is broader than was the case at 63°. All mixtures the gross compositions of which are represented by points falling within the area *A* are completely liquid at 90°. The heterogeneous field *B* has also increased in size. All mixtures represented

FIG. 2.



initially by points within the area *B* give a liquid the composition of which is represented by a point on the liquidus, together with a solid solution represented by the corresponding point on the solidus. Mixtures represented by points within the triangle *E* always give saturated solutions of tin and silver in mercury; thus the liquids given by the mixtures the compositions of which are *d* and *g* are identical, and their composition is represented by the intersection of the boundary curves of the field *A*. It will be evident from the above that mixtures represented by points falling within any of the other areas give the substances represented by

the angular points of the triangle in which the points fall. It is probable that the cross-section of the solidus is not a straight line as shown in the figure, but as yet the actual shape of the solidus is not known as accurately as is the case with the liquidus. This point will be referred to again.

In the same way that we obtained the results of table Ia from table I, we can get those of table IIa from table II.

TABLE IIa.

Point on Diagram.	No. of atoms of silver to 100 atoms of mercury.	No. of atoms of tin to 100 atoms of mercury.
"Silver"	0.33	—
<i>d</i>	1.28	26.3
<i>e</i>	0.56	4.4
<i>f</i>	0.93	14.9
<i>g</i>	1.22	26.1
<i>h</i>	1.06	18.8
<i>k</i>	1.12	20.0
"Tin"	—	25.0

Special attention was devoted to the diagram at 166.5°, the results being as follows:

TABLE III.

Temp. 166.5°±0.5.

Gross composition.			Composition of liquid phase.			Point on diagram.
Ag.	Sn.	Hg.	Ag.	Sn.	Hg.	
	Pure silver		1.13	—	98.87	"Silver"
58.3	25.0	16.7	3.11	57.6	39.3	<i>l</i>
57.1	14.3	28.6	3.57	32.7	63.7	<i>m</i>
50.0	12.5	37.5	2.73	25.6	71.7	<i>n</i>
44.8	6.6	48.6	3.20	13.9	82.9	<i>o</i>
41.7	41.7	16.6	2.80	66.2	31.0	<i>p</i>
40.0	26.7	33.3	3.02	44.3	52.7	<i>q</i>
39.9	39.9	20.2	2.82	64.1	33.1	<i>r</i>
29.9	4.9	65.2	1.41	4.6	94.0	<i>s</i>
28.8	40.0	31.2	2.70	54.4	42.9	<i>t</i>
20.0	53.5	26.5	2.95	62.5	34.5	<i>u</i>
15.1	10.1	74.8	2.80	13.0	84.2	<i>v</i>
14.3	57.1	28.6	2.60	65.0	32.4	<i>w</i>
9.6	77.1	13.3	1.60	66.6	31.8	<i>x</i>
8.7	78.3	13.0	2.73	67.1	30.2	<i>y</i>
	Pure tin		—	65.6	34.4	"Tin"

The cross-section of the thermal diagram at 166.5° is given in Fig. 3.

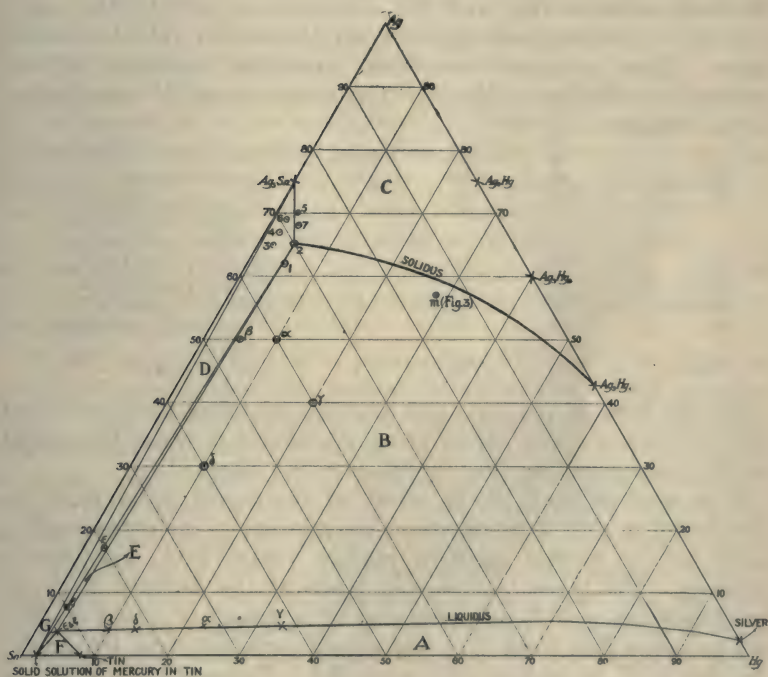
TABLE IV.

Temp. $214.0^{\circ} \pm 0.5$.

Gross composition.			Composition of liquid phase.			Point on diagram.
Ag.	Sn.	Hg.	Ag.	Sn.	Hg.	
	Pure silver		2.3	—	97.7	"Silver."
50.0	40.0	10.0	4.8	72.7	22.5	α
50.0	45.0	5.0	4.3	86.0	9.7	β
40.0	40.0	20.0	5.1	61.4	33.5	γ
30.0	60.0	10.0	4.0	82.3	13.7	δ
17.8	80.3	2.4	3.9	93.2	2.9	ϵ
8.0	90.0	2.0	3.8	93.2	3.0	ζ
	Pure tin		—	92.0	8.0	"Tin."

The cross-section of the thermal diagram at 214° is given in Fig. 4. It is similar to those obtained at lower temperatures, and the remarks made there apply here also.

FIG. 4.



The Solidus.

The position and shape of the solidus has not been determined as accurately as the liquidus. The method by which its approxi-

mate position has been found is as follows: From measurements of the vapour pressures of silver amalgams, which are being carried out by one of us, it is known that Ag_3Hg_4 is solid and stable at 300° , since it has at that temperature a vapour pressure considerably lower than that of mercury. From this it appears that a mixture of mercury and silver gives rise to Ag_3Hg_4 and a saturated solution of silver in mercury. Hence the solidus passes through the point Ag_3Hg_4 , the corresponding point on the liquidus at any temperature giving the concentration of the solution of silver in mercury at that temperature. During the present series of measurements it was found that the mixture *m* (Fig. 3) gave rise to a small amount of liquid phase. Therefore the solidus lies slightly above *m*. A mixture corresponding with $(\text{Ag}_3\text{Sn})_2\text{Hg}$ gave absolutely no indication of a liquid phase at 166° . Hence the solidus at 166° passes through Ag_3Hg_4 , slightly above *m*, and somewhat below $(\text{Ag}_3\text{Sn})_2\text{Hg}$. In the same way at 214° its position is the same thus far, but the left hand end was investigated in the following way: Mixtures corresponding with the compositions given by the points 1, 2, 3 . . . 7 were made up, and were heated to 214° for several hours. These mixtures were then examined carefully for the presence or absence of liquid. The compositions of these points are as follows:

	Ag.	Sn.	Hg (at. %)	Presence or absence of liquid.
(1).....	62	33	5	Plenty of liquid.
(2).....	65	30	5	If present, amount of liquid was extremely small.
(3).....	65	33	2	Certainly gave liquid.
(4).....	67	31	2	Certainly gave liquid.
(5).....	70	27	3	Gave no liquid.
(6).....	69	29	2	Very small amount of liquid.
(7).....	68	28	4	Gave no liquid.

In the case of (5), (6), and (7) the mixtures were heated at 250° for twelve hours before being introduced into the thermostat at 214° , thus ensuring that equilibrium was attained.

It is evident that, if the *whole* of the liquid phase could be withdrawn in each determination, the position of the corresponding point on the solidus could be readily found with considerable accuracy. For if we had $(m+n)$ grams of the mixture *A* in the reaction tube, and if this gave rise to *m* grams of liquid *B*, then the corresponding point *C* on the solidus could be found by producing *BA* to *C*, so that $n \times CA = m \times BA$. Unfortunately it is not possible to withdraw the whole of the liquid phase. It may be possible to determine the amount of liquid phase left behind in the reaction tube in the following manner. A small weighed amount of gold is added to the metals in the reaction tube. After the liquid

phase has been withdrawn a gold assay is made of the substance left behind in the tube. If it was known that all the gold passed into the liquid phase, the result of the gold assay would permit of the calculation of the amount of liquid phase left behind, and from this we should be able to determine the amount of solid which was in equilibrium with the total amount of liquid phase. Then by calculation the position could be found of the corresponding point on the solidus. This method we hope to test. It is possible that the solidus is more convex upwards than is represented in the figures. This point will be settled later on.

Discussion of the Results.

It is evident from inspection of the figures that all the diagrams are of the same type. The most striking feature is the rapid increase in size of the fields *A* and *B* with rise in temperature, so that at 166° the liquid field *A*, which at 63° reached less than one-tenth of the distance across the diagram towards the tin side, now reaches three-quarters of the way across.

Even more rapid is the falling off in the maximum content of tin in the solidus as the temperature is lowered; thus at 90° the solidus still extends about two-fifths of the distance across the diagram, but at 63°, only 27° lower, it reaches only one-sixth of this distance, and contains not more than just over 2 per cent. of tin. It is thus evident that at room temperature the tin capable of dissolving in the crystals of "*Arbor Dianae*," Ag_3Hg_4 , must be quite negligible in amount, in accordance with the conclusions previously arrived at.

It will be evident from a comparison of Figs. 1—3 that an amalgam such as that represented by *q*, which is solid at room temperature, will partly liquefy at some temperature between 63° and 90°, and will gradually become more liquid as the temperature is raised. This seems to be a satisfactory explanation of the fact that breaks occur in the cooling curves. Although there is no reason for assuming the existence of two sets of equilibria, since the liquidus is of similar shape at all the temperatures investigated, yet for all practical purposes it remains true that we have to deal with a rapid change in the equilibria involved in most amalgams when these are heated through the temperatures lying between 70° and 100°.

The advance of the liquidus curve up the ternary diagram towards the Ag corner may be readily inferred from the way in which the solubility of silver in mercury increases with the temperature, together with the known behaviour of the binary liquids

on the Ag-Sn side of the diagram. This advance scarcely affects the type of equilibrium involved, and it is of no practical importance on account of the still more rapid increase in volatility of mercury.

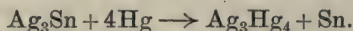
The experiments arising out of this and the previous communications are being continued in this laboratory.*

Summary.

(1) The experimental data in a previous communication have been confirmed.

(2) Further experiments on the unique property of "ageing" have been described.

(3) The equilibrium diagrams have been extended to temperatures up to 214°. It has been shown that, although theoretically continuous throughout, for practical purposes they may be grouped into two classes—those above about 70° containing a large proportion of solid solution, those below containing negligible amounts only; thus the summarised equation of amalgamation at room temperature is:



The experiments presented above were commenced by one of us (R. A. J.) in 1910, and continued by the other throughout the present year. We desire to express our indebtedness to Dr. James W. McBain for constant advice throughout the investigation.

In conclusion our thanks are due to the Research Fund Committee of the Chemical Society for a grant towards the purchase of materials and apparatus.

THE CHEMICAL LABORATORY,
UNIVERSITY OF BRISTOL.

* Further experiments, which will be included in a later communication, have shown the hypothesis that ageing may be due to catalytic action of the iron or products of iron introduced during the filing to be untenable.

CCXXXV.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XIX. The Rotation of Certain Derivatives of Lactic Acid.*

By THOMAS STEWART PATTERSON and WILLIAM COLLINS FORSYTH
(Carnegie Research Scholar).

FROM the stereochemical point of view, lactic acid and its derivatives are of very considerable interest on account of the simple constitution of the molecule, especially, of course, the fact that it contains only one asymmetric carbon atom. We have thought it desirable, therefore, to prepare three of these derivatives of active lactic acid in order to examine their rotations through a fairly wide range of temperature, and also dissolved in two liquids, which, as experience has shown, differ greatly, as a rule, in their action.

Our optically active material was made by three different methods, which may be briefly indicated. The first consisted in resolving ordinary lactic acid by means of morphine (Irvine, T., 1906, **89**, 935). The syrupy lactic acid with which we commenced had a specific gravity of 1.21, and showed a slight positive rotation. By boiling this syrup with ten times its weight of water for six hours and then titrating with sodium hydroxide solution it was found that a quantity of lactic acid was formed, equal to 91.3 per cent. of the weight of the syrup. One hundred and ninety c.c. of this lactic acid were boiled under reflux with 2280 c.c. of water. To half of this solution 350 grams of morphine were added, whilst the other half—adopting a principle suggested by Pope and Peachey in the resolution of tetrahydroquinaldine (T., 1899, **75**, 1066)—was neutralised with the equivalent quantity, 46.3 grams, of sodium hydroxide. The solutions were mixed, and on cooling and then further evaporation three crops of crystals of morphine *l*-lactate were obtained, weighing in all 400 grams. The product was dissolved in 1400 c.c. of boiling water, and then an equal volume of alcohol added to the filtered solution. The substance which separated when the solution cooled was again crystallised in the same way, and ultimately a yield of about 83 per cent. of the theoretical was obtained. This is not quite so high as is recorded by Irvine, but it was obtained by the use of only half the proportional quantity of morphine. The pure morphine *l*-lactate was dissolved in hot water, the morphine precipitated by ammonia, and removed by filtration. Two-thirds of the filtrate were boiled with zinc oxide until the ammonia had all

disappeared, and, after filtration, the solution was added to the other third, the mixture being then concentrated by evaporation and set aside to crystallise, when zinc ammonium *l*-lactate was obtained. This had a rotation of $\alpha_D^{19.5}$ (100 mm.) 0.487° , $c=8.07$, which gives for the specific rotation $+6.03^\circ$, whereas Purdie quotes $+6.06^\circ$ at 20° .

We also prepared active zinc ammonium lactate by the resolution of the zinc ammonium salt exactly according to Purdie and J. Wallace Walker (T., 1895, **67**, 618, 619; see also Purdie, T., 1893, **63**, 1143), and from 500 c.c. of lactic acid syrup 160 grams of zinc ammonium lactate were obtained. The specific rotation of this first crop of crystals was $[\alpha]_D^{20} +5.94^\circ$, $c=8$; α_D^{20} (200 mm.) 0.95° , so that the substance was practically pure, and on recrystallisation it gave $[\alpha]_D^{20} +6.05^\circ$. The yield thus obtained was rather more than three times that recorded by Purdie, and the mother liquor was found to have a rotation of $+0.78^\circ$ (100 mm.) at 20° , so that it still contained *l*-lactate in excess. The lactic acid with which this last experiment had been carried out was a different sample from that first used; it was obtained, through a local dealer, from Merck, and its rotation in a 100 mm. tube was found to be $+4.36^\circ$ at 20° , which is very much higher than the rotation usually found for ordinary lactic acid, and is considerably higher than the rotation of pure active lactic acid, this, of course, being due to the fact that *l*-lactide is present, and has a high positive rotation. Commercial lactic acid often contains a slight preponderance of one or other of the active forms; but it is said to be only seldom that the *d*- or *l*-variety occurs in large excess (Meyer and Jacobson, "Lehrbuch der organischen Chemie," 2nd Ed., Vol. I., Part II, 560), and as this sample had so high an activity we thought it worth while to ascertain in what proportions the two constituents were present. Some of the acid was therefore converted into the ethyl ester by the method described by Purdie and Williamson (T., 1896, **69**, 828). This, after careful purification by distillation with a Sydney Young fractionating column under a pressure of 13 mm., boiled at $47-49^\circ$, and gave α_D^{18} (100 mm.) $+4.5^\circ$, whilst Purdie and Williamson found the observed rotation of the pure ester at 14° to be 11.5° , and Purdie and Irvine (T., 1899, **75**, 485) found the observed rotation of their specimen at 8° to be 11.2° . The rotation of our preparation was therefore almost half that of the pure ester, so that the original lactic acid must have contained about 75 per cent. of *l*-acid and only 25 per cent. of *d*-acid (see Frankland and MacGregor, T., 1893, **63**, 1028; Harden, T., 1901, **79**, 610). We then obtained a number of samples of lactic acid from different sources

in order, if possible, to find another quantity with a high activity. As is well known, the rotation of lactic acid syrup itself is due chiefly to the presence of lactide, and in order to ascertain whether the rotation of the syrup is a good guide as to the quantity of active acid it contains we took 4 c.c. of each sample, placed it in a 50 c.c. flask, added to this 15 c.c. of a solution of 7 grams of sodium hydroxide in 45 c.c. of water, and then filled up to the mark with water. The rotation of the resulting solution of sodium lactate was then examined. The results were as follows:

Number of sample.	<i>t</i> .	Observed rotation of syrup (100 mm.).	Observed rotation of sodium salt solution (400 mm.).
1.	17.5°	+4.36°	+1.746°
2.	17.5	-0.65	-0.381
3.	17.5	+0.30	+0.164
4.	13.0	+5.30	+2.126

It will be noticed that the numbers for the rotation of the sodium salt solution are roughly proportional to those showing the rotation of the syrup, the rotations in both cases being of the same sign. It will be observed, further, that the last specimen showed an even higher rotation than that already referred to. We therefore obtained a quantity of this acid, which must have contained over 80 per cent. of *l*-lactic acid, and from it we prepared the zinc salt as follows: Three hundred grams, or 250 c.c., of the syrup were added to a mixture of 142 grams of zinc oxide and 3000 c.c. of hot water, and the whole boiled for some time until a neutral reaction was obtained. The liquid was decanted from a slight excess of zinc oxide, and allowed to crystallise. Inactive zinc lactate separated from the hot solution, and was collected. This preparation was repeated six times. The filtrate, on concentration, gave a deposit of active zinc lactate, which was crystallised several times, on each occasion from about six times its weight of boiling water, and in this way some 300 grams of pure zinc *l*-lactate were obtained with ease. If a fairly active specimen of lactic acid can be obtained, this is probably the simplest method of preparing an active salt. In the course of the crystallisation a considerable amount of partly active zinc lactate was obtained, from which zinc ammonium *l*-lactate was prepared. From 450 c.c. of the partly active lactic acid syrup and 250 grams of the partly active zinc lactate—which had a rotation of about 0.9° (400 mm.), *t*=13°, *c*=4; the pure salt would have α_D 1.4° in these circumstances—212 grams of pure active zinc ammonium *l*-lactate were obtained.

One difficulty which occurs in work on lactic acid is the fact that the rotation of its salts, such as the zinc and the zinc ammonium salts, is only low, and it is difficult, by using this criterion, to determine the purity of any sample with much accuracy. We

therefore adopted the plan of dissolving the salt in ammonia solution instead of in water. This had two advantages: in the first place, the zinc ammonium salt decomposes in water, separating out some less soluble zinc lactate, and this is prevented by the use of ammonia solution; in the second place, the presence of the ammonia considerably raises the rotation of the salt. Our ammonia solution was prepared by making up 300 c.c. of concentrated ammonia solution (D 0.880) to a litre with distilled water. The specific gravity of this solution by the Westphal balance was found to be 0.971, and the strength of the solution by titration with oxalic acid, using phenolphthalein as indicator, was 3.99*N*. Four grams of pure zinc ammonium lactate, made up to 50 c.c. with this solution, gave $\alpha_D^{17.2}(400 \text{ mm.}) + 3.232^\circ$, whereas the rotation in water was only 1.948° ; thus by using ammonia solution the rotation is almost doubled.

Methyl l-lactate was prepared by the sulphuric acid method of Purdie and Williamson (T., 1896, **69**, 828) and Purdie and Irvine (T., 1899, **75**, 484), except that the crude ester was distilled through a Sydney Young fractionating column of 15 disks, under a pressure of about 13 mm., when it boiled at 40° and at $48^\circ/16 \text{ mm.}$ This is a considerable advantage, and saves the repeated and very wasteful distillation of the ester otherwise necessary. Methyl lactate, it may be noted, is fairly easily volatile along with methyl alcohol, the alcohol recovered in our first distillation (from an ordinary Wurtz flask) having a rotation of $+0.36^\circ$ ($l=400 \text{ mm.}$), and, when distilled with the column, gave a residue of 4 c.c. having a rotation of $+4.2^\circ$, this quantity being, therefore, equivalent to 2 c.c. of the pure ester.

Rotation of Methyl l-Lactate.

The rotation of this preparation was then examined at various temperatures, with the following results:

t°	-75.0	-62.0	-51.0	-8.6	+16.7	17.8
d	1.2042	1.1882	1.1752	1.1205	1.0971	1.0960
$\alpha_D^{20}(100 \text{ mm.})$..	+6.596	6.726	6.861	8.396	8.882	8.950
$[\alpha]_D^{20}$	+5.479	5.661	5.838	7.45	8.10	8.17
$[M]_D^{20}$	+5.696	5.887	6.071	7.75	8.42	8.49
t°	35.4	56.0	78.8	96.7	125.0	
d	1.0751	1.0518	1.0256	1.0048	0.9725	
$\alpha_D^{20}(100 \text{ mm.})$...	9.332	9.808	10.238	10.536	10.824	
$[\alpha]_D^{20}$	8.68	9.32	9.98	10.48	11.13	
$[M]_D^{20}$	9.03	9.70	10.38	10.90	11.57	

Methyl l-Lactate in Nitrobenzene.

The nitrobenzene had been distilled under diminished pressure.

$p=9.877$:

t	16.0	18.9	36.2	37.9	56.5	81.9	104.5	141.0
d	1.1920	1.1910	1.1735	1.1717	1.1525	1.1270	1.1021	1.0670
α_D^{25} (160 mm.)	+1.856	1.876	1.836	1.846	1.850	1.856	1.850	1.846
$[\alpha]_D^{25}$	9.854	9.947	9.902	9.98	10.16	10.42	10.63	10.95
$[M]_D^{25}$	10.24	10.35	10.30	10.38	10.56	10.84	11.05	11.39

Methyl l-Lactate in Tetrachloroethane (Acetylene Tetrabromide).

The tetrachloroethane was distilled under 13 mm. pressure, and boiled at 115—117°.

$p=9.937$:

t	-7.8	+17.6	39.7	69.8	94.3	120
d	2.5825	2.5292	2.4840	2.4220	2.3706	2.3160
α_D^{25} (160 mm.)	-3.146	-1.903	-0.998	-0.032	+0.738	+1.376
$[\alpha]_D^{25}$	-7.66	-4.73	-2.53	-0.083	+1.96	+3.74
$[M]_D^{25}$	-7.97	-4.92	-2.63	-0.086	+2.04	+3.89

Methyl l- α -acetoxypropionate was prepared by boiling methyl *l*-lactate with excess of acetyl chloride. The product of the reaction was distilled under diminished pressure, using a Sydney Young column. It boiled at 68—70°/13 mm. and 171—172° at atmospheric pressure.

Rotation of Methyl l- α -Acetoxypropionate.

t	-7.4	+19.8	43.0	59.5	83.2	114.0	141.0
d	1.1199	1.0885	1.0620	1.0435	1.0165	0.9808	0.9500
α_D^{25} (50 mm.)	+30.394	29.552	28.78	28.224	27.448	26.514	25.694
$[\alpha]_D^{25}$	54.26	54.28	54.20	54.09	54.03	54.05	54.08
$[M]_D^{25}$	79.23	79.25	79.14	78.98	78.89	78.93	78.96

Methyl l- α -Acetoxypropionate in Nitrobenzene.

$p=10.14$:

t	0.3	19.2	45.4	65.0	83.5	110.0	141.0
d	1.2105	1.1919	1.1650	1.1445	1.1262	1.10	1.0690
α_D^{25} (100 mm.)	+7.336	6.914	6.364	6.126	5.908	5.708	5.514
$[\alpha]_D^{25}$	+59.78	57.20	53.88	52.77	51.76	51.18	50.88
$[M]_D^{25}$	+87.30	83.52	78.66	77.05	75.58	74.73	74.29

Methyl l- α -Acetoxypropionate in Tetrachloroethane.

$p=10.035$:

t	17.6	39.8	54.7	76.4	91.3	119.0	139.3
d	2.5262	2.4817	2.4520	2.4078	2.3772	2.3220	2.2705
α_D^{25} (160 mm.)	+19.294	18.886	18.632	18.234	18.066	17.722	17.428
$[\alpha]_D^{25}$	+47.56	47.37	47.32	47.17	47.34	47.53	47.80
$[M]_D^{25}$	+69.45	69.18	69.08	68.87	69.11	69.40	69.81

Methyl l- α -methoxypropionate was prepared exactly according to the method of Purdie and Irvine (T., 1899, **75**, 485), and was finally distilled with a column, under diminished pressure. It boiled at 40°/18 mm. and 130—131°/760 mm.

Rotation of Methyl l- α -Methoxypropionate.

t°	-16.6	16.4	41.2	51.1	78.4	110.0	130.0
d	1.0361	0.9986	0.9704	0.9590	0.9283	0.8916	0.8685
α_D^{25} (30 mm.) ...	+32.107	29.112	27.28	26.414	24.528	22.826	21.932
$[\alpha]_D^{25}$	+103.3	97.16	93.71	91.81	88.28	85.35	84.16
$[M]_D^{25}$	+121.9	114.7	110.6	108.3	104.2	100.7	99.31

Methyl l- α -Methoxypropionate in Nitrobenzene.

$p=9.802$:

t°	16.6	41.7	70.5	92.8	119.0
d	1.1843	1.1590	1.1290	1.1066	1.0795
α_D^{25} (160 mm.) ...	+16.496	15.55	14.544	13.756	12.928
$[\alpha]_D^{25}$	+88.82	85.27	82.17	79.25	76.40
$[M]_D^{25}$..	+104.8	100.7	97.18	93.53	90.36

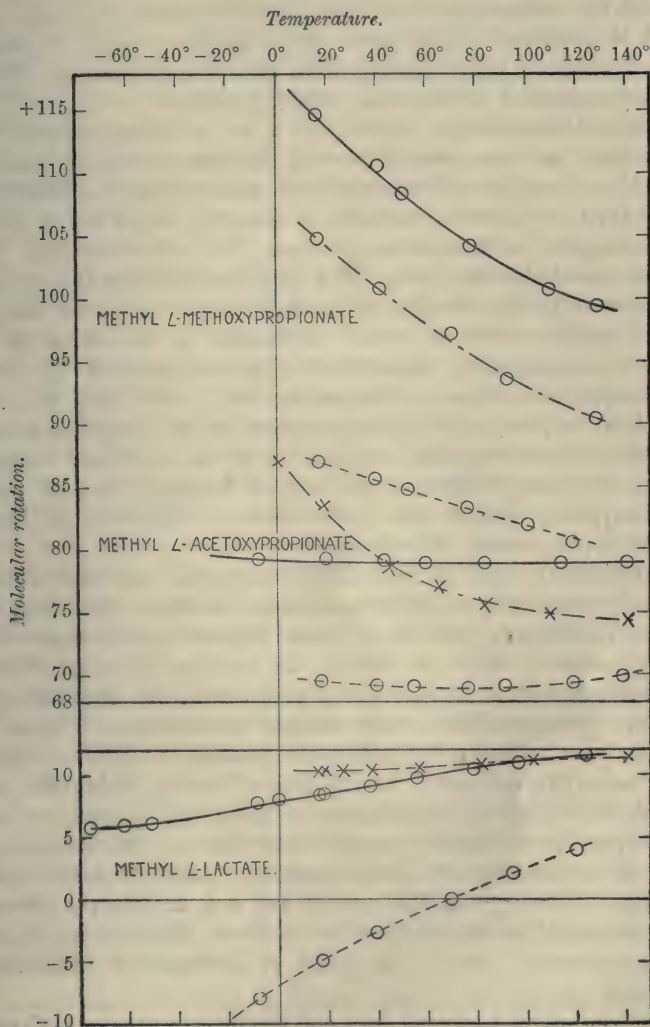
Methyl l- α -Methoxypropionate in Tetrachloroethane.

$p=10.0616$:

t°	16.7	39.8	52.5	77.0	101.0	119.0
d	2.4860	2.4390	2.4135	2.3630	2.3140	2.2760
α_D^{25} (100 mm.) ...	+18.444	17.798	17.448	16.766	16.156	15.620
$[\alpha]_D^{25}$	+73.69	72.52	71.85	70.52	69.40	68.21
$[M]_D^{25}$	+86.96	85.59	84.78	83.22	81.91	80.48

The diagram represents our experimental data. The relative rotations of methyl *l*-lactate, methyl *l- α* -acetoxypropionate, and methyl *l- α* -methoxypropionate at a single temperature were, of course, already known, but the influence of temperature change on them has not previously been studied. The full lines in the diagram represent the behaviour of the homogeneous active substances, and it will be observed that the influence of temperature change in the three cases is comparatively slight; thus the rotation of methyl *l*-lactate only changes some 6° within a temperature range of fully 200°; nevertheless, the curve has two interesting characteristics. First, at the higher temperatures it tends, apparently, towards a maximum value, and second, since there appears to be a point of inflexion somewhere about -10°, it is possible that at lower temperatures than those we have reached, a minimum rotation also may exist for methyl *l*-lactate. The importance of maximum and minimum rotations and points of inflexion has been discussed by one of us in a recent paper (this vol., p. 145), so that the matter need not be further dealt with here.

When methyl *L*-lactate is converted into methyl *L*- α -acetoxypropionate the change is accompanied by a great rise of rotation, but the rotation of the acetyl compound is very little affected by



Temperature-rotation curves for derivatives of l-lactic acid in the homogeneous condition (full lines), in solution in nitrobenzene, $p=10$ (dash-dash-dot curves), and in tetrabromoethane, $p=10$ (dotted curve).

change of temperature within the ordinary limits. A minimum rotation appears to exist, however, at a temperature in the neighbourhood of 40° , and this accounts for the comparative invaria-

bility of the rotation with change of temperature, since it is, of course, in the neighbourhood of a maximum or a minimum that da/dt is a minimum.

When the acetoxy-group is replaced by a methoxy-group a compound is obtained which has a still higher rotation, a rotation which diminishes fairly rapidly with rise of temperature. Now it has been suggested in the paper already referred to (*loc. cit.*) that the temperature-rotation curves for a set of closely-related compounds such as these may all be of the same type, the exchange of certain groups for others merely producing a shift of the fundamental type of curve to the right or the left, to the top or bottom of the diagram, accompanied, however, by individual but minor differences and characteristics. It is thus possible that the minimum which occurs in the rotation of methyl *l*-lactate at a low temperature of about -80° or -100° represents a condition of the molecule corresponding with that which is assumed by methyl *l*- α -acetoxypropionate at a temperature of $+40^{\circ}$ and in methyl *l*- α -methoxypropionate at a temperature in the neighbourhood of 200° , and this affords some explanation of the fact that whilst the rotation of methyl lactate increases on heating, that of methyl *l*- α -acetoxypropionate is but little altered, and that of methyl *l*- α -methoxypropionate diminishes.

The rotation of each of these active compounds was also examined in nitrobenzene and in tetrabromoethane solution. Previous work with ethyl tartrate had shown that whereas nitrobenzene has a very pronounced effect in raising the rotation of ethyl tartrate, tetrabromoethane is almost equally powerful in diminishing it. Therefore, it appeared to be of interest to ascertain in what way the rotation of these other active compounds would be influenced by the same two solvents. In the case of methyl *l*-lactate it seems tolerably clear that in nitrobenzene solution the minimum rotation would occur at a higher temperature than in the homogeneous ester. It is probable also that a maximum rotation would exist in this same solution, but the curves are not sufficiently extensive to decide whether at a higher or a lower temperature than in the homogeneous ester. A point of inflexion is indicated at about 60° .

Nitrobenzene as a solvent does not produce so great an elevation of the rotation of methyl *l*-lactate as of that of ethyl tartrate, and similarly tetrabromoethane, although it considerably diminishes the rotation of the lactate, does so to a less extent than in the case of ethyl tartrate. No point of inflexion is apparent in this curve, so that a minimum rotation would be expected to occur at a still lower temperature than in the homogeneous ester. From the curves it is hardly possible to say whether the maximum rotation

of this solution will lie at a lower temperature than that of the homogeneous ester or of the ester dissolved in nitrobenzene.

The influences of nitrobenzene and of tetrabromoethane on the rotation of methyl *l*- α -methoxypropionate are, on the whole, somewhat similar to their effects on the rotations of the other two esters examined. Tetrabromoethane brings about the greater lowering of rotation, but the nitrobenzene curve does not cut that for the homogeneous ester. We may point out, however, although it may seem to be arguing on somewhat slender premisses, that whereas the curve for the homogeneous ester and that in nitrobenzene solution for methyl *l*-lactate occurs at a fairly high temperature of about 100° , a similar intersection takes place for methyl *l*- α -acetoxypropionate at about 40° , and therefore it may possibly be that a corresponding intersection in the case of methyl α -methoxypropionate should occur at a still lower temperature. For this ester also it may be noticed that the three curves are more widely separated from each other, thus suggesting that as the rotation of the compound becomes greater the sensitiveness of the molecular asymmetry to the influences of different solvents becomes greater also; in other words, the change produced in passing from one solvent to another is greater for the methyl *l*- α -methoxypropionate with its high rotation than for the methyl *l*-lactate with its low rotation. The three curves in this case appear to be tending towards a minimum value, but it is obviously difficult or impossible to say what the relative position of these minima would be.

The effect of the two solvents is much the same on the three different esters, thus supporting the view, which is steadily gaining ground, that the relative influence of a set of solvents on several active compounds is closely similar.

On the whole, it may be said that these curves, although perhaps they do not present any very striking confirmation or support of the ideas suggested in the paper referred to, are quite in harmony with these suggestions. It is a little unfortunate that the comparatively easy volatility of the substances examined has somewhat limited their investigation.

In conclusion, we have to thank Messrs. T. and H. Smith, of Edinburgh, for the loan of a considerable quantity of morphine and for presenting us with another quantity of it for use in the experiments recorded, whilst we desire also to acknowledge that some of the rotation data quoted in the paper were obtained with a polarimeter placed at the disposal of one of us by the Carnegie Trustees for the Universities of Scotland.

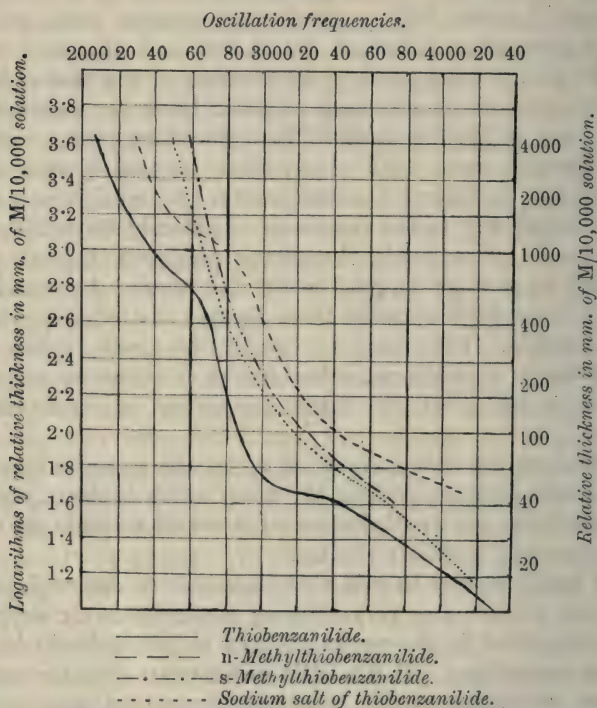
CCXXXVI.—*The Tautomerism of Thioanilides.*

By PERCY MAY.

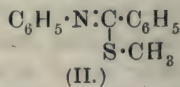
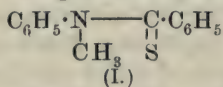
IN order to decide which of the two possible tautomeric formulæ better represents thiobenzanilide itself, the two methyl derivatives have been examined and their properties compared with those of the parent substance.

The absorption curve of the parent substance closely resembles

FIG. 1.



that of the *N*-methyl derivative (I). The curves for the sodium salt and the *S*-methyl derivative (II) are practically identical, but differ in character from, and show less general absorption* than, those of the parent substance and *N*-methyl derivative.



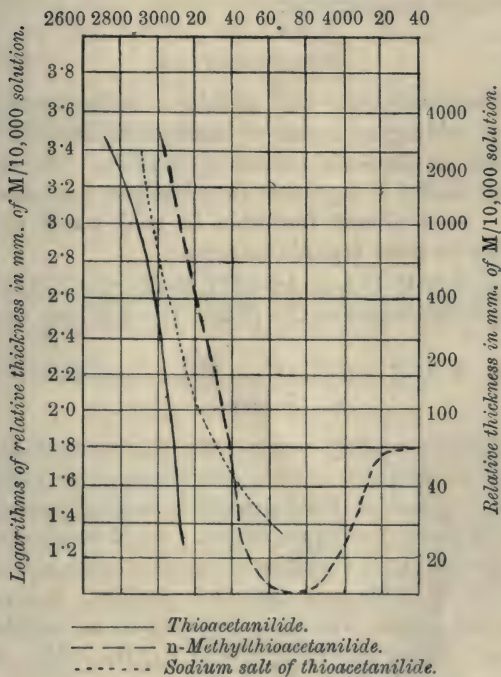
* In comparing the general absorption, only the upper portion of the curves, where there are neither bands nor incipient bands, is considered.

The spectroscopic evidence, therefore, is in favour of the usual thioketone formula for thiobenzanilide.

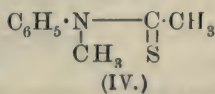
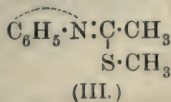
On the other hand, the sodium salt and *S*-methyl derivative (III) of thioacetanilide show greater general absorption than the *N*-methyl derivative (IV). This is in accordance with the observation that substances containing double bonds in the conjugated

FIG. 2.

Oscillation frequencies.



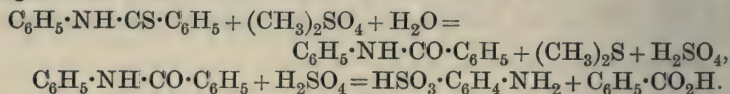
position show greater general absorption than isomeric compounds containing the double bonds in the unconjugated position:



In the case of thioacetanilide, the spectroscopic evidence is not very conclusive, but here also it appears to favour the thioketone structure.

On attempting to methylate thiobenzanilide in neutral solvents decomposition always took place, the sulphur being eliminated as

methyl sulphide. When the reaction was carried out in hot xylene solution the chief product of the reaction was sulphanilic acid. The small amount of water present in the solvent brings about this complete decomposition, which probably takes place in two stages:



In some solvents the first stage, formation of methyl sulphide, is complete at room temperature.

EXPERIMENTAL.

S-Methylthiobenzanilide was obtained as a white, crystalline precipitate on adding an excess of methyl sulphate to a solution of thiobenzanilide in aqueous sodium hydroxide. On crystallisation from aqueous alcohol it separates in colourless, fine needles, melting at 63—64°. It is almost insoluble in cold water or alkali, but readily soluble in most organic solvents:

0.1350 gave 0.3640 CO_2 and 0.0717 H_2O . $\text{C}=73.53$; $\text{H}=5.90$.

$\text{C}_{14}\text{H}_{13}\text{NS}$ requires $\text{C}=73.94$; $\text{H}=5.77$ per cent.

Action of Methyl Sulphate on Thiobenzanilide in Neutral Solvents.

Methyl sulphate readily reacts with thiobenzanilide in neutral solvents, such as benzene, xylene, nitrobenzene, or methyl alcohol; for example, 5 grams of thiobenzanilide were dissolved in xylene, and 5 grams of methyl sulphate added. A red colour was produced, and on warming a rapid evolution of methyl sulphide occurred, and a solid separated. This was collected, purified, and recrystallised from hot water, and was then identified as sulphanilic acid. (Found, after drying at 120°, $\text{C}=41.3$; $\text{H}=4.55$. $\text{M.W.}=174$. $\text{C}_6\text{H}_7\text{O}_3\text{NS}$ requires $\text{C}=41.6$; $\text{H}=4.05$ per cent. $\text{M.W.}=173$.)

Methyl sulphide is also formed when the reaction is carried out in the other solvents mentioned above, and when methyl iodide reacts with a methyl-alcoholic solution of thiobenzanilide.

N-Methylthiobenzanilide.

Methylbenzanilide was obtained by the action of benzoyl chloride on a pyridine solution of methylaniline, and was finally obtained in large, transparent crystals melting at 58°. Four grams of phosphorus pentasulphide, 2 grams of phosphorus trisulphide, and 6 grams of methylbenzanilide were powdered, mixed, and heated for half-an-hour on the water-bath. The product was extracted

with ether, and the crude substance so obtained extracted with cold alcohol, which dissolved out some dark-coloured impurities. The residue was crystallised from ether, and recrystallised from aqueous alcohol, from which it separates in small, yellow cubes, melting at 90—91°:

0.1485 gave 0.1570 BaSO₄. S=14.52.

C₁₄H₁₃NS requires S=14.11 per cent.

My thanks are due to the Research Fund Committee of the Chemical Society for a grant towards the expenses of the investigation, and to Dr. Smiles, who kindly supplied me with the thiobenzanilide.

UNIVERSITY OF LONDON,
UNIVERSITY COLLEGE.

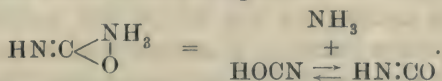
CCXXXVII.—*Mechanism of the Decomposition of Carbamide and Biuret by Heat, and of the Formation of Ammelide.*

By EMIL ALPHONSE WERNER.

IN continuation of the work recently published (this vol., p. 1010), further experiments have now been completed, the results of which afford a full explanation of the mechanism of the different changes under consideration, and supply further evidence in support of the theories which have been put forward by the author.

Considering the number of communications which have appeared from time to time on the decomposition of carbamide by heat, it is rather remarkable that no careful quantitative study of the changes appears ever to have been made; to supply this want, and to clear up certain undoubtedly misleading statements on record, the present investigation was carried out.

It has been shown (*loc. cit.*) that when pure dry carbamide is heated slightly above its melting point it undergoes rapid dissociation, ammonia and cyanic acid being formed as sole volatile products, in accordance with the equation:



Cyanuric acid is produced as a result of the polymerisation of a portion of the cyanic acid originally present in the keto-form,

whilst biuret is simultaneously formed by the action of cyanic acid on unchanged carbamide, further evidence of which has been obtained from the study of the action of heat on biuret, described later on. If the heating is prolonged, and particularly if the temperature is raised to 190—200°, a small quantity of ammelide is formed, the production of which has been recognised for a long time by different observers, although no importance apparently has been attached to its existence as a product of the decomposition of carbamide by heat. It will be shown, however, in the following that the formation of ammelide has an interesting significance when dealing with the explanation of the mechanism of the different changes, and its production calls for immediate comment before giving the detailed results of the quantitative study of the whole process.

Some years ago Hantzsch and F. Hofmann (*Ber.*, 1905, **38**, 1013) examined the action of heat on carbamide, and whilst they showed that no cyamelide is formed, they obtained a sparingly soluble substance resembling the latter in appearance, which they concluded to be tricyanocarbamide, $C_3N_3(NH \cdot CO \cdot NH_2)_3$, the possibility of the substance being ammelide was apparently overlooked, in spite of the fact that all the properties of the compound as described by Hantzsch are in agreement with that substance. After a careful investigation of the substance, the details of which are given in the experimental part of the paper, the author is forced to the conclusion that no such substance as tricyanocarbamide is produced by the action of heat on either carbamide or biuret, ammelide alone being the very sparingly soluble substance which is formed in both cases, and the origin of its production will be dealt with under the decomposition of biuret.

I. *Quantitative Study of the Decomposition of Carbamide by Heat.*

The general plan adopted in all the experiments was as follows: Five grams of pure dry carbamide were heated in a thin-walled test-tube, 18 cm. long by 2.5 cm. wide; whilst the tube was maintained in a nearly horizontal position, the heat was applied directly with a small flame. After removal of the sublimate, the residue was thoroughly extracted with cold water to the volume of 100 c.c.; the biuret formed was estimated colorimetrically in an aliquot portion of the solution by the aid of the well-known "biuret reaction"; this was found to give very satisfactory results, even in the presence of cyanuric acid and carbamide. The residue from the aqueous extract was dried and weighed, the total cyanuric acid present in this residue and in the aqueous solution was

estimated by titration with *N*/10-sodium hydroxide solution, as described in a previous paper (*loc. cit.*), and the ammeline was determined by difference, or in some cases by direct weighing after removal of the cyanuric acid by solution in warm water.

The results of four experiments are given below:

TABLE I.

Expt. I. Heated very slowly; heat removed as soon as opalescence set in. Time, 12 minutes.		Expt. II. Heated at a moderate rate until appearance of opalescence. Time, 7—8 minutes.	
	Per cent.		Per cent.
Loss ($\text{NH}_3 + \text{HCNO}$)	8.40		12.20
NH_4OCN (in sublimate)	0.58		0.21
Biuret.....	18.26		24.50
Cyanuric acid	3.35		5.93
Ammeline	0.83		3.94
	<hr/> 31.42		<hr/> 46.78
Unchanged carbamide (by difference)...	68.58		53.22

Expt. III. Heated rather rapidly until appearance of opalescence. Time, 5 minutes.		Expt. IV. Heated very rapidly; heat continued, after appearance of opalescence, until gas evolution had practically ceased. Time, 6—7 minutes.	
	Per cent.		Per cent.
Loss.....	15.00		19.00
NH_4OCN	0.06		0.42
Biuret.....	16.66		10.25
Cyanuric acid	9.16		15.34
Ammeline	3.30		8.46
	<hr/> 44.18		<hr/> 53.47
Unchanged carbamide (by difference)...	55.82		46.53

In experiments I and II the temperature did not rise beyond 180° , in III and IV the temperature reached 205° as a maximum, but was most of the time about 195° .

The following results represent the proportions of biuret and cyanuric acid respectively, calculated on the amount of carbamide actually decomposed in each experiment:

TABLE II.

	Expt. I.	Expt. II.	Expt. III.	Expt. IV.
Biuret	58.1	52.4	37.7	19.1 per cent.
Cyanuric acid	10.6	12.7	20.7	28.6 „ „

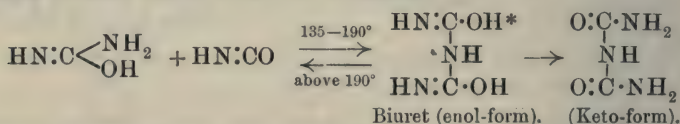
Thus slow heating at a temperature well below the melting point (190°) of biuret represents the best conditions for the production of this substance, which is in agreement with the view already given regarding the theory of its formation; rapid heating, as

might naturally be expected, hastens the polymerisation of cyanic acid, a factor which militates against biuret formation.

II. Quantitative Study of the Decomposition of Biuret by Heat.

The decomposition of biuret by heat is generally disposed of by the simple statement that it gives off ammonia and yields cyanuric acid; whilst this even is only partly true, the primary action of heat on biuret, which is of particular interest, appears to have been hitherto quite overlooked.

It has been recently pointed out by the author (*loc. cit.*) that when biuret is heated in a test-tube to the point of decomposition it furnishes a crystalline sublimate composed of carbamide and ammonium cyanate, thus proving that cyanic acid must accompany the ammonia as a volatile product. It is now shown, from the results recorded below, that the first effect of the action of heat on biuret just above its melting point is to cause its dissociation into the products from which it was generated, namely, carbamide and cyanic acid, from which it follows that the formation of biuret, during the action of heat on carbamide, is a reversible change, in accordance with the equation:



Since carbamide is regenerated at a temperature considerably above the limit of its stability, it dissociates rapidly into ammonia and cyanic acid, the latter quickly polymerising; this prevents a state of equilibrium, corresponding with the above equation, from persisting for any length of time; nevertheless, by heating biuret for a few minutes just above its melting point, and afterwards cooling rapidly, as much as 30 per cent. of carbamide may be readily extracted from the residue. Ammelide is also formed during the decomposition of biuret,[†] and, as will be presently shown, the latter is, in fact, a necessary precursor to the formation of ammelide during the decomposition of carbamide. Before dealing with the theory of its origin, the quantitative results of the action of heat on biuret are given in the following table.

Four grams of anhydrous biuret were used in each experiment,

* The above change being established, it is obvious that the question of the constitution of biuret is opened up thereby; this matter, together with the constitution of carbamide, is at present under investigation, and the results shall form the subject of a future communication.

† This has already been noticed by Hantzsch (*loc. cit.*), although he has considered the substance to be tricyanocarbamide.

and the estimation of the products formed was carried out as described under carbamide; the numbers given below represent percentages of the weight of biuret taken.

TABLE III.

	Expt. I. Heated at 195—198° until pasty mass formed. Time, 5 minutes.	Expt. II. Heated until gas evolution ceased (195—200°). Time, 7 minutes.	Expt. III. Heated rapidly (195—205°) until residue solid Time, 10 minutes.
Volatile ($\text{NH}_3 + \text{HNCO}$)	8.25 per cent.	13.75 per cent.	23.12 per cent.
Sublimate	4.95 "	6.37 "	3.75 "
Cyanuric acid	37.24 "	37.08 "	57.96 "
Ammelide	3.57 "	5.87 "	5.37 "
Biuret (unchanged).....	12.34 "	10.40 "	0.77 "
	<hr/> 66.35 "	<hr/> 73.47 "	<hr/> 90.97 "
Carbamide, generated...	33.65 "	26.53 "	9.03 "

The carbamide was not directly determined, but its presence in quantity was proved by precipitation as nitrate, and by other tests, in a portion of the aqueous extract of the residues from experiments I and II. The following experiment was made with the main object of determining the carbamide formed.

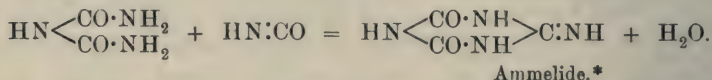
Eight grams of biuret were heated, in a short, wide-mouthed tube immersed in a bath of glycerol, for ten minutes at 192°. The carbamide was estimated by precipitation as nitrate; whilst this was bound to give a result below the real value, it was sufficiently accurate for the purpose required. The residue after heating was extracted with 30 c.c. of cold water; 20 c.c. of this solution gave on addition of 15 c.c. of concentrated colourless nitric acid 2.88 grams of carbamide nitrate, the composition of which was checked by titration with *N*-sodium hydroxide solution.

Results Obtained.

Expt. IV.	
Carbamide.....	26.42 per cent.
Cyanuric acid	24.85 "
Ammelide	2.88 "
Biuret (unchanged)	22.40 "
	<hr/> 76.55

Neither the sublimate nor the loss by volatilisation was determined. As already pointed out in the case of carbamide, rapid heating largely increases the yield of cyanuric acid by hastening polymerisation of the cyanic acid set free; this is not accompanied by any increase in the amount of ammelide formed, the maximum yield of which is probably reached under the conditions of expt. II, table III, so far as the decomposition of biuret is concerned.

When anhydrous biuret is heated, the evolution of a small quantity of aqueous vapour is noticeable as soon as decomposition sets in, a phenomenon which is not observable in the case of carbamide until the temperature reaches about 155° , below which no ammelide is formed. The evolution of water is, in fact, a by-product of the formation of ammelide, which, the facts seem to indicate, originates from the interaction of biuret and cyanic acid in accordance with the equation:



Another explanation of its origin might be found in its possible formation as a result of the direct interaction of ammonia and cyanuric acid, thus:

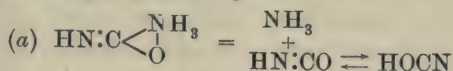


A direct experiment to test this gave a negative result, no ammelide being formed by heating cyanuric acid to 160 — 180° in a current of ammonia. Moreover, since ammonia is continuously evolved during the decomposition of biuret, an increase in the yield of ammelide might naturally be expected to accompany an increase in the production of cyanuric acid; this, however, is not the case, as shown in expt. III, table III; on the contrary, all other conditions being equal, rapid removal of the biuret from the sphere of action is accompanied by a fall in the yield of ammelide, which is in agreement with the theory of its formation given above. This also explains why a much larger quantity of ammelide is formed by the action of heat on carbamide, under suitable conditions, as compared with the action of heat on biuret; this is well shown in the results of expt. IV, table I, where the yield of ammelide was equal to 15.8 per cent. of the weight of carbamide decomposed. In accordance with the theory of its formation it is obvious that the yield of ammelide cannot be other than small, since the temperature at which it appears to be most rapidly formed lies about the point at which biuret is rapidly decomposed and at which cyanic acid undergoes very rapid polymerisation.

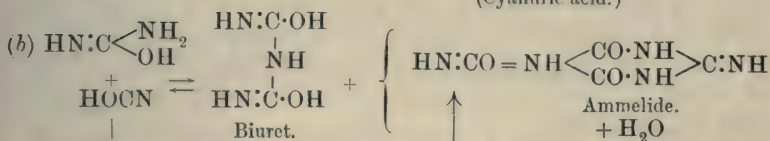
Thus the mechanism of the series of changes which accompany the progressive action of heat on carbamide may be illustrated by the following scheme, in which it is seen that the phenomenon of

* This is the tautomeric form of $\text{HN} \begin{array}{c} \text{CO} \cdot \text{NH} \\ \text{CO} \cdots \text{N} \end{array} \text{C} : \text{NH}_2$, which is also used to express the constitution of ammelide, since this substance possesses feeble basic, in addition to pronounced acidic, properties.

dissociation and the instability and reactivity of nascent cyanic acid are the active agents in the process:



↓
By polymerisation = (HNCO)₃
(Cyanuric acid.)



Whilst the cyclic formula (a) is used to represent the constitution of carbamide in the first stage of the decomposition, it is not unlikely that the direct dissociation of carbamide into ammonia and cyanic acid by heat is also accompanied by a change in constitution represented by the hydroxylic formula (b); this alteration in structure would probably be determined by the presence of a negative agent, such as cyanic or cyanuric acid in the fused product.

EXPERIMENTAL.

Preparation and Identification of Ammelide.

Before any definite conclusions could be drawn from the experimental results, it was necessary to place beyond doubt the nature of the sparingly soluble substance formed in the experiments described, since Hantzsch (*loc. cit.*) has described as tricyanocarbamide, $\text{C}_3\text{N}_3(\text{NH} \cdot \text{CO} \cdot \text{NH}_2)_3$, a product having all the characteristics of ammelide.

The opalescence which suddenly appears in the fused product after carbamide has been heated for a short time above 150° is due to the separation of this substance; it was readily freed from the other products by extracting the latter with warm water. Nitrogen estimations were made in four different preparations, with the following results:

(a) From action of heat on carbamide. No purification beyond thorough extraction with warm distilled water:

0.198 gave 73.7 c.c. N_2 at 15° and 768.5 mm. $\text{N} = 44.29$.

(b) Same as (a). Purified by crystallisation from hot 5 per cent. hydrochloric acid solution:

0.1475 gave 54.9 c.c. N_2 at 18° and 763 mm. $\text{N} = 43.38$.

(c) Same as (a). Purified by dissolving in sodium hydroxide solution, and, after filtration, precipitating with acetic acid:

0.1065 gave 39.9 c.c. N_2 at 17° and 766.5 mm. $\text{N} = 43.78$.

(d) From action of heat on biuret. Purified as in (c):

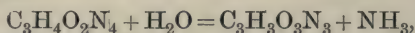
0.1365 gave 50.9 c.c. N_2 at 17° and 769 mm. $N=43.82$.

$C_3H_4O_2N_4$ (ammelide) requires $N=43.75$ per cent.

$C_6H_9O_3N_9$ (tricyanocarbamide) requires $N=49.41$ per cent.

Hydrolysis of the compound gave the following results:

0.5 Gram heated with 15 per cent. hydrochloric acid for two hours at $140-150^\circ$ in a sealed glass tube was completely hydrolysed with formation of ammonia and cyanuric acid as the sole products; no carbamide was formed, and there was no evolution of carbon dioxide on opening the tube. The change is in agreement with the equation:



and proves, together with the analytical results, that the very sparingly soluble substance formed in all the experiments is ammelide only.

Colorimetric Estimation of Biuret.

This was carried out in the following manner: A standard solution of convenient strength was prepared by dissolving 0.5 gram of pure anhydrous biuret in about 200 c.c. of distilled water, to which 50 c.c. of *N*-sodium hydroxide solution were added; freshly precipitated copper hydroxide* was then introduced, until, after thorough shaking, a small quantity of the hydroxide remained undissolved; the solution was then diluted with distilled water to 500 c.c., well mixed, and allowed to remain until the slight excess of copper hydroxide had completely subsided. The clear, purple-red solution so obtained could then be removed by means of a pipette as required; 25 c.c. ($=0.025$ of biuret), diluted with water to 100 c.c. in a Nesslerising cylinder, were found to give a suitable colour tint for comparison with the solutions obtained from the present experiments.

The results of two check experiments will suffice to give an idea of the accuracy which may be obtained in the estimations:

A. Biuret(present in 100 c.c. of solution) $=0.095$. Found= 0.09448 .

B. Biuret(with equal weights of carbamide and cyanuric acid also present in solution) $=0.175$. Found= 0.1739 .

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* Prepared by adding a slight excess of sodium hydroxide to copper sulphate solution, without any further treatment.

CCXXXVIII.—*The Absorption Spectra of Various Derivatives of Pyridine, Piperidine, and Piperazine in Solution and as Vapours.*

By JOHN EDWARD PURVIS.

THE absorption spectra of solutions of pyridine, α - and β -picolines, and piperidine have been studied by Hartley (T., 1885, **47**, 685), and by Baker and Baly (T., 1907, **91**, 1122), and they found one large band in pyridine and α - and β -picolines, but none in piperidine.

The author has given accounts of the absorption spectra of the vapours and alcoholic solutions of pyridine and some of its derivatives (*Proc. Camb. Phil. Soc.*, 1907, **14**, 381; 1908, **14**, 436, 568; T., 1909, **95**, 294). It was proved that whereas the vapours of pyridine and α -picoline exhibit a considerable number of fine, narrow bands, the vapours of 2:6- and 2:4-dimethylpyridines and 2:4:6-trimethylpyridine showed none of these finer bands, and that there was only a single large absorption band comparable with the solution band. It was also shown that the vapour of piperidine had a considerable number of fine, narrow bands, although the solution had none.

The vapours of several of the substances then examined have since been investigated, and also the solutions and vapours of other derivatives of pyridine, piperidine, and piperazine. These substances were: 2-dipyridyl (solution and vapour); 4-phenylpyridine (solution and vapour); 3:5-dichloropyridine (vapour); 2:3:5-trichloropyridine (vapour); 3:4:5-trichloropyridine (vapour); 2:3:4:5-tetrachloropyridine (vapour); tetrachloro-2-aminopyridine (vapour); pentachloropyridine (vapour); methyl trichloropicolinate (vapour); 2:3:4-trichloropicolinamide (vapour); 2:3:4-hexachloropicoline (vapour); piperidine (neutral and acid solutions); 4-phenylpiperidine (solution and vapour); nitroso-piperidine (solution and vapour); benzoylpiperidine (solution and vapour); and piperine (vapour). The solutions of a number of these substances have been examined before (*loc. cit.*), so that their vapours only were now investigated. The piperazine substances examined were: piperazine (solution and vapour); α - and β -dimethylpiperazines (solution and vapour); dibenzoyl- α - and β -dimethylpiperazines (solutions).

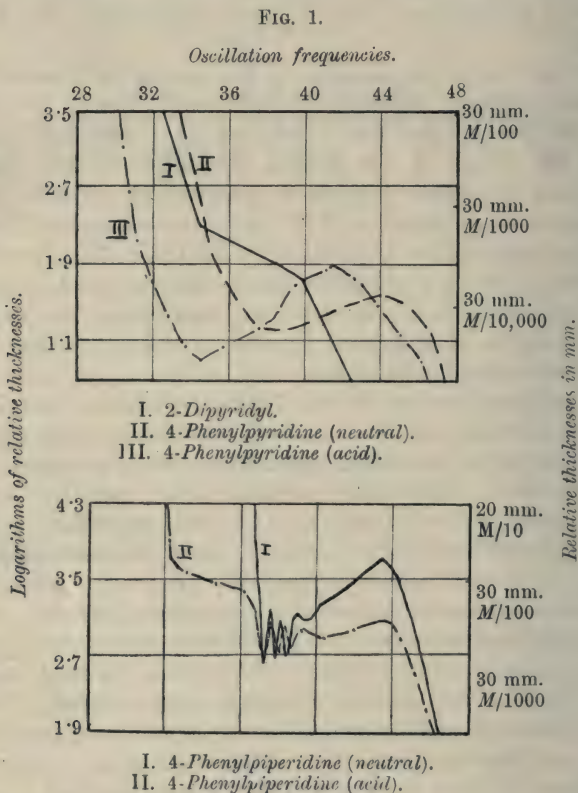
The apparatus and methods of working have been described before.

Solutions.

2-Dipyridyl, $C_{10}H_8N_2$.—The curve (Fig. 1, upper curves I) shows that the pyridine band has almost disappeared, and there is

only a rapid extension of the transmitted rays between $1/\lambda$ 3450 and $1/\lambda$ 4000 (λ 2897— λ 2498). It may be mentioned that Hartley (*loc. cit.*) found a very weak band in dipyridyl between λ 2568 and λ 2310.

4-Phenylpyridine, $C_{11}H_9N$.—The curve (Fig. 1, upper curves II) shows a wide band, the head of which is at $1/\lambda$ 3900 (λ 2563). It is not unlike the solution band of pyridine (*loc. cit.*). There is no trace of the seven solution bands of benzene as described by



Hartley and Huntingdon (*Phil. Trans.*, 1879, **170**, i, 257), and by Baly and Collie (*T.*, 1905, **87**, 1332). The large pyridine band covers the region of these seven bands, which extend between $1/\lambda$ 3690 (λ 2709) and $1/\lambda$ 4290 (λ 2330). The acid solution of the substance shows a marked change in the absorption; the band (Fig. 1, upper curves III) is shifted more towards the red end, and is more persistent than that of the neutral solution. This result is similar to that observed by Baker and Baly and by the

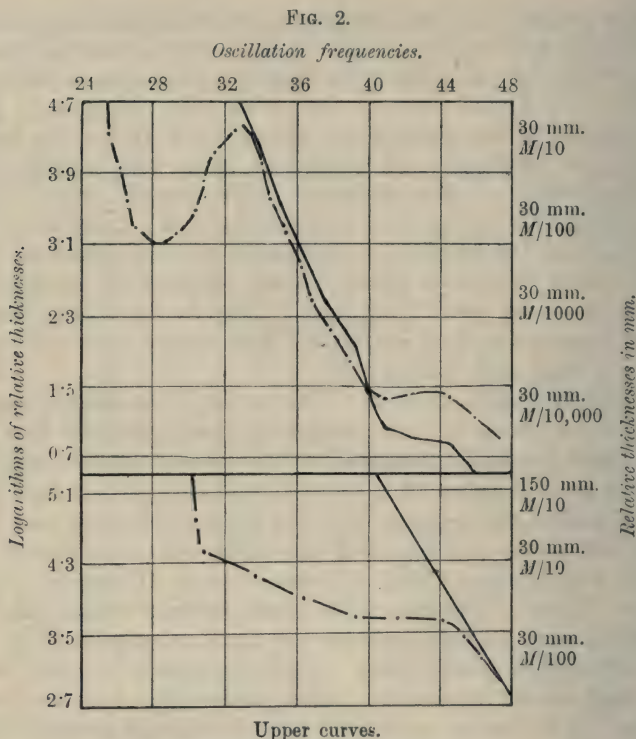
author in neutral and acid solutions of other pyridine compounds (*loc. cit.*). There is no appearance of the solution bands of benzene.

Piperidine, $C_5H_{11}N$.—Alcoholic solutions were first examined by Hartley (*loc. cit.*) and then by the author (*loc. cit.*), but no bands were observed in the ultra-violet regions. The author has studied slightly acid solutions, and compared these with equimolecular neutral solutions of the substance. The curves (Fig. 2, lower curves) show that in the acid solutions there is a rapid absorption of the rays as the thickness is increased between about $1/\lambda$ 3100 and $1/\lambda$ 4400 (λ 2720— λ 2240). This appears to indicate the presence of a very weak band, and it may be mentioned that the narrow vapour bands described by the author (*loc. cit.*) range between λ 2637 and λ 2438.

4-Phenylpiperidine, $C_{11}H_{15}N$.—The curve of the neutral solution (Fig. 1, lower curves I) is remarkable in that it exhibits four weak bands, which gradually disappear as the concentration is increased, and their place is taken by a single large band. These four bands are not unlike the benzene solution bands, but they are much weaker and closer together, and they differ also in position. The slightly acid solution (Fig. 1, lower curves II) shows striking changes. Three of the four weak bands become weaker, and they are shifted very slightly towards the more refrangible side. The most refrangible fourth band almost disappears, as well as the large band which appears at greater concentrations in the neutral solution. It is also to be noticed that the line of general absorption is shifted considerably towards the red end, and that the rapid extension of the transmitted rays between $1/\lambda$ 3300 and $1/\lambda$ 3600 (λ 3028 and λ 2776) may probably indicate the presence of a large weak band.

Nitrosopiperidine, $C_5H_{10}O_2N$.—The curve (Fig. 2, upper curve—dash and dot) shows a strong band, the head of which is at $1/\lambda$ 2850 (λ 3500), and probably connected with the nitroso-group and the colour of the substance. There is also a somewhat rapid extension of the transmitted rays between about $1/\lambda$ 3950 and $1/\lambda$ 4400 (λ 2530— λ 2270), beyond which the photographic plates are not susceptible. This may be the beginning of a large band which extends into the extreme ultra-violet regions. In any case, nitrosopiperidine differs from piperidine, for no solution band has been noticed in the latter compound (*loc. cit.*).

Benzoylpiperidine, $C_{12}H_{15}ON$.—The curve (Fig. 2, upper curve—continuous) shows no band, and in this respect it resembles the solution of piperidine. There may be traces of a rapid extension of the rays from about $1/\lambda$ 4150 (λ 2408) into the extreme ultra-violet regions, not unlike that in nitrosopiperidine.



Piperazine, $C_4H_{10}N_2$.—Alcoholic solutions of various strengths were examined, but no bands were detected. The following numbers indicate the regions where general absorption begins:

	λ .
$M/5-100$ mm. thickness general absorption begins at	2565
120	2575
140	2580
158	2590
$M/10-10$	2260
20	2320
30	2360
40	2430
60	2460
88	2540

The transparency of the solutions of piperazine and its compounds described below is very remarkable. In this direction it is comparable with neutral solutions of piperidine.

2-Dimethylpiperazine, $C_6H_{14}N_2$.—Alcoholic solutions of various strengths showed no band. The following numbers give the regions where general absorption begins in $M/100$ -solutions:

					λ .
$M/100$ -10 mm. thickness	general absorption begins at				2200
30	"	"	"	"	2270
50	"	"	"	"	2300
70	"	"	"	"	2400
90	"	"	"	"	2420
120	"	"	"	"	2450
160	"	"	"	"	2480

3-Dimethylpiperazine, $C_6H_{14}N_2$.—No bands were observed in alcoholic solutions of various strengths, and the following numbers give the regions where general absorption begins in $M/10$ -solutions:

					λ .
$M/10$ -8 mm. thickness	general absorption begins at				2300
16	"	"	"	"	2410
24	"	"	"	"	2480
40	"	"	"	"	2550
80	"	"	"	"	2600
120	"	"	"	"	2640
140	"	"	"	"	2800
156	"	"	"	"	2830

1:4-Dibenzoyl-2-dimethylpiperazine, $C_{20}H_{22}O_2N_2$.—This substance is not quite so soluble in alcohol as the 3-dimethyl compound. A saturated solution of about $M/140$ -strength was investigated, but no bands were observed. The following numbers give the regions where general absorption begins:

					λ .
$M/140$ -10 mm. thickness	general absorption begins at				2800
20	"	"	"	"	2840
30	"	"	"	"	2870
$M/1400$ -10	"	"	"	"	2570
20	"	"	"	"	2670
30	"	"	"	"	2730
$M/14,000$ -10	"	"	"	"	2140
20	"	"	"	"	2270
30	"	"	"	"	2380

1:4-Dibenzoyl-3-dimethylpiperazine, $C_{20}H_{22}O_2N_2$.—No bands were observed in solutions of various strengths. The following numbers give the regions where general absorption begins:

					λ .
$M/100$ -10 mm. thickness	general absorption begins at				2780
20	"	"	"	"	2830
30	"	"	"	"	2850
90	"	"	"	"	2885
130	"	"	"	"	2930
$M/1000$ -10	"	"	"	"	2590
20	"	"	"	"	2690
30	"	"	"	"	2730
$M/10,000$ -10	"	"	"	"	2200
20	"	"	"	"	2400
30	"	"	"	"	2470

Vapours.

The vapours were examined in a 200 mm. tube at various temperatures and pressures, as described in the earlier investigations.

2-Dipyridyl, $C_{10}H_8N_2$.—At about 175° the rays were transmitted to λ 2144, and at about 185 — 190° to λ 2250, but they were slightly weak between λ 2660 and λ 2550. There was no appearance of any of the series of narrow bands found in pyridine vapour by the author (*loc. cit.*). The single weak band is comparable with the equally weak solution band.

4-Phenylpyridine, $C_{11}H_9N$.

t° .	Pressure in mm.	
80	890	The rays were transmitted to λ 2144.
85	896	„ „ absorbed between λ 2540— λ 2350, and then feebly transmitted to λ 2270.
90	900	The rays were transmitted to λ 2600, beyond which there was complete absorption.

There was no appearance of any of the vapour bands of benzene and its homologues described by Hartley (*Phil. Trans.*, 1907, A, 208, 475) or of pyridine vapour described by the author (*loc. cit.*). The single band is comparable with the solution band of pyridine, except in position.

3:5-Dichloropyridine, $C_5H_3Cl_2N$.—The following numbers give the wave-lengths, measured on the more refrangible edges, of the bands observed in the vapour.

Abbreviations: w=weak; v.w.=very weak; str.=strong; mod. str.=moderately strong; narr.=narrow.

30° .		35° .	
814 mm.		830 mm.	
λ .		λ .	
2866 v. w.		2866 w.	
2863 „		2863 w.	
2859 „			
2858 w.		2858 mod. str.	
2852 mod. str.		2852 str.	
2849 v. w., narr.		2849 v. w., narr.	
2845 mod. str.		2844 str.	
2843 „		2843 mod. str.	
2835 w.			
2833 str.		2833 str., wide	
2829 str.			
2827 w., narr.		2827 „ „	
2823 „ „			
2821 str.			
2820 w., narr.			
2818 str.		2819 „ „	
2814 mod. str., narr.		2814 w., narr.	
		2812 mod. str.	
2811 mod. str.			
2806 w., narr.		2806 w., wide	
		30°.	35°.
		814 mm.	830 mm.
		λ .	λ .
		2803 w., narr.	2805 w., wide
		2800 mod. str.	
		2795 w.	The rays were then fairly well absorbed to λ 2650, and then transmitted to λ 2220.
		2790 mod. str.	
		2786 „	
		2780 w.	
		2776 w.	
		2764 w.	
		2753 w.	14 bands and 1 large band.
		2746 mod. str.	
		2740 w.	
		The rays were then feebly absorbed to about λ 2650, and then transmitted to λ 2200.	
		30 bands and 1 large band.	

40°. 850 mm. λ.	80°. 910 mm. λ.	100°. 946 mm. λ.
2898 v.w.	B {	2912 v.w.
2895 w.		2908 „
2879 v.w.		2904 „
2875 „		2898 w.
2869 „		2895 mod. str.
2864 w.		2890 v.w.
2862 w.	The rays were then completely absorbed from λ 2885.	
2858 mod. str.		
2856 w., narr.		
2855 „ „		
2850 mod. str.		
2845 w., narr.	The rays were then completely absorbed from λ 2920.	
2843 „ „		
2841 „ „		

The rays were then absorbed to about λ 2540, and then transmitted to λ 2240.
14 bands and 1 large band.

At the higher temperatures and pressures the bands became stronger and wider, and more bands appeared on the less refrangible side; and at the same time, the more refrangible bands gradually disappeared. Between the extreme temperatures of 30° and 100° the total number of narrow bands was forty-one, and there was a large band on the more refrangible side of these narrow bands, which is well marked at 35° and 45°.

On comparing the bands with those of pyridine (*loc. cit.*) there is no very close resemblance, and the former are weaker and shifted more towards the red end. The large band on the more refrangible side of the narrow bands is comparable with that of pyridine, except that it is also shifted more towards the red. The total number of bands found in the vapour of pyridine was forty-five, and one large band on the more refrangible side of the narrower bands.

2:3:5-Trichloropyridine, $C_5H_2Cl_3N$.—The absorption bands of the vapour of the substance were investigated in a tube 200 mm. long. Abbreviations as before (see p. 2290).

The bands do not appear to have a very close resemblance to those of pyridine. They are also much weaker, and shifted more towards the red end. There are two large groups, A' and B', and these are fairly comparable with the group A of 3:5-dichloropyridine. As in the other substances, at the higher temperatures and pressures, the narrower bands disappear, and a large band makes its appearance on the more refrangible side; this is particularly well shown at the temperatures of 60° and 75°. The

	20°. 759 mm. λ.	30°. 783 mm. λ.	45°. 829 mm. λ.	60°. 859 mm.
<i>A'</i>	2910 v.w. 2907 " 2903 " 2900 mod. w. 2895 v.w. 2891 " 2888 " 2883 " 2878 " 2871 " 2858 " 2855 " 2848 mod. w.	2914 w. 2911 mod. w. 2909 w. 2906 mod. w. 2904 v.w. 2900 mod. str. 2895 v.w. 2891 " 2887 w. 2883 w. 2876 w. 2874 w. 2869 w. 2863 w. 2857 v.w. 2853 w. 2847 mod. str. 2844 v.w. 2812 mod. str.	2916 v.w. 2914 mod. str. 2912 v.w. 2910 mod. str. 2909 " 2906 " 2903 w. 2900 str. 2895 w. 2891 w. 2888 v.w. 2883 str. 2876 mod. str. 2874 " 2870 w. 2863 w. 2858 w. 2853 w. 2846 mod. str.	The rays were completely absorbed between λ 2940 — λ 2680, and then transmitted to λ 2330. 75°. 889 mm. The rays were absorbed between λ 2970 — λ 2630, and then transmitted to λ 2380. 90°. 920 mm. The rays were transmitted to λ 3000, beyond which there was complete absorption.
<i>B'</i>	The rays were then transmitted to λ 2140. 13 bands.	The rays were then transmitted to λ 2140. 19 bands.	The rays were then absorbed to λ 2750, whence they were transmitted to λ 2290. 19 bands and 1 large band.	

fourteen narrower bands are fewer than those in the vapour of 3:5-dichloropyridine.

3:4:5-Trichloropyridine, $C_5H_2Cl_3N$.

<i>t</i> °.	Pressure in mm.	
60	860	The rays were feebly absorbed between λ 2840—λ 2710, and then transmitted to λ 2250.
75	890	The rays were absorbed between λ 2880—λ 2620, and then transmitted to λ 2280.
90	920	The rays were transmitted to λ 2920, and then there was complete absorption.

There was no appearance of any of the narrow bands observed in 2:3:5-trichloropyridine. The single large band is comparable with that found in the solution and in the solution of pyridine (*loc. cit.*). It is clear, therefore, that although the number of chlorine atoms is the same in both isomerides, their orientation determines the absorption to a very large extent.

2:3:4:5-Tetrachloropyridine, C₅HCl₄N.

<i>t</i> °.	Pressure in mm.	
70	870	The rays were feebly absorbed between λ 2920— λ 2730, and then transmitted to λ 2300.
80	900	The rays were fairly well absorbed between λ 2940— λ 2700, and then transmitted to λ 2380.
90	930	The rays were absorbed between λ 2970— λ 2670, and then transmitted to λ 2450.
100	946	The rays were absorbed between λ 3000— λ 2600, and then feebly transmitted to λ 2560.

Again, therefore, there were no narrow bands found in the vapour of this compound, and the large band is comparable with that of the solution band (*loc. cit.*).

Tetrachloro-2-aminopyridine, C₅H₂N₂Cl₄.

<i>t</i> °.	Pressure in mm.	
120	773	The rays were fairly well absorbed between λ 3000— λ 2800, and then transmitted to λ 2430.
130	773	The rays were absorbed between λ 3100— λ 2770, and then transmitted to λ 2500.
140	773	The rays were absorbed between λ 3200— λ 2740, and then transmitted to λ 2550.
160	773	The rays were transmitted to λ 3300, beyond which there was complete absorption.

Pentachloropyridine, C₅Cl₅N.

120	764	The rays were feebly absorbed between λ 2980— λ 2790, and then transmitted to 2250.
125	764	The rays were moderately well absorbed between λ 2980— λ 2780, and then transmitted to λ 2380.
130	764	The rays were almost completely absorbed between λ 3000— λ 2760, and then transmitted to λ 2450.
135	764	The rays were absorbed between λ 3010— λ 2740, and then transmitted to λ 2480.
145	764	The rays were absorbed between λ 3040— λ 2720, and then transmitted to λ 2480.
165	764	The rays were absorbed between λ 3080— λ 2650, and then transmitted to λ 2530.
175	764	The rays were completely absorbed from λ 3100.

All the narrow bands found in pyridine have completely disappeared, and a large band remained in each of these substances, comparable with the solution band of each (*loc. cit.*).

Methyl 2:3:4-Trichloropicolinate, C₇H₄O₂NCl₃

<i>t</i> °.	Pressure in mm.	
100	760	The rays were very weakly absorbed between λ 2900— λ 2750, and then transmitted to λ 2260.
110	760	The rays were fairly well absorbed between λ 2990— λ 2700, and then transmitted to λ 2420.
120	760	The rays were almost completely absorbed between λ 3010— λ 2670, and then transmitted to λ 2470.
130	760	The rays were completely absorbed between λ 3050— λ 2620 and then transmitted to λ 2530.
140	760	The rays were completely absorbed from λ 3070.

2:3:4-Trichloropicolinamide, $C_6H_3ON_2Cl_3$.

190	770	The rays were moderately well absorbed between λ 3200— λ 2900, and then transmitted to λ 2450.
200	770	The rays were well absorbed between λ 3250— λ 2800, and then transmitted to λ 2530.

2:3:4-Hexachloropicoline, $C_6HNC l_6$.

130	770	The rays were well absorbed between λ 2940— λ 2630, and then transmitted to λ 2540.
140	770	The rays were transmitted to λ 2960, beyond which there was complete absorption, except that the Cd line 2573 was visible.
150	770	There was complete absorption of the rays from λ 2980.

So that in all these three substances there was no appearance of any narrow bands, and the large band of each is comparable with the solution band found previously (*loc. cit.*).

4-Phenylpiperidine, $C_{11}H_{15}N$.

t° .	Pressure in mm.	
80	760	The rays were transmitted to λ 2190.
90	760	„ „ „ „ λ 2230, but there was a distinct weakening between λ 2470— λ 2330.
100	760	The rays were well absorbed from λ 2550 to the series of Cd lines λ 2329— λ 2265 which were just visible.
110	760	The rays were absorbed from λ 2650.
120	760	„ „ „ „ λ 2700.

That is to say, there are no series of bands like those found either in the vapour of benzene and its homologues by Hartley, nor like those found in piperidine by the author (*loc. cit.*). There are merely strong indications of a band comparable with the large solution band found in the greater thicknesses, and there is no appearance of the four very weak bands found in the more dilute solutions.

In connexion herewith the author has examined very thin films of the substance in the manner described in previous communications to see whether such films absorbed the light like the solution. Four very weak bands were found which are comparable with the solution bands; but, as in previous comparisons also, they are shifted slightly more towards the red end. The heads of these four weak bands are at about λ 2697, λ 2665, λ 2627, λ 2556; or, in oscillation frequencies, at $1/\lambda$ 2706, $1/\lambda$ 3750, $1/\lambda$ 3805, $1/\lambda$ 3911.

Nitrosopiperidine, $C_5H_{10}ON_2$.

t° .	Pressure in mm.	
30	752	The rays were transmitted to λ 2144.
45	822	" " " " λ 2500, but the two Cd lines 2194 and 2144 were just visible.
60	852	The rays were transmitted to λ 2650.
75	882	" " " " λ 2750.
100	928	The rays were moderately well absorbed between λ 3800— λ 3450, and then transmitted to λ 2850.

The observations, therefore, prove that all the thirty-seven vapour bands of piperidine vapour described by the author (*loc. cit.*) have completely disappeared. The single band extending into the visible regions, like that of the solution band, is connected with the nitroso-group, and therefore with the colour of the compound. It shows so signs of being resolved into a series of narrow bands.

Benzoylpiperidine, $C_{12}H_{15}ON$.

t° .	Pressure in mm.	
100	765	The rays were transmitted to λ 2190.
120	765	" " " " λ 2270.
150	765	" " " " λ 2580.
170	765	" " " " λ 2680.
190	765	" " " " λ 2750.

So that, like the vapour of nitrosopiperidine, all the vapour bands of piperidine have disappeared, and no other band was observed.

Piperine, $C_8H_{10}N \cdot C_{12}H_9O_3$.—The vapour was examined at various temperatures. At about 165° there appeared a large band between λ 3250 and λ 2830; and there was no trace of any of the narrower bands found in the vapour of piperidine. With regard to the solutions, Hartley (*Phil. Trans.*, 1885, **176**, 471) found a wide band between λ 360 and λ 270, and Dobbie and Fox (*T.*, 1912, **103**, 1193) confirmed this. The latter observers also showed that this band was similar to that of piperic acid, and they draw the conclusion that substances the molecules of which are composed of two nuclei will give the characteristic band of the unsaturated one. The author discusses this remark later.

Piperazine, $C_4H_{10}N_2$.

t° .	Pressure in mm.	
100	765	The rays were transmitted to λ 2144.
120	765	" " " " λ 2400.
130	765	" " " " λ 2550.
160	765	There were three weak somewhat diffuse bands at λ 2703, λ 2700, and λ 2696, and the rays were then transmitted to λ 2580.
175	765	These three weak bands became a little stronger and the measurements are λ 2704, λ 2700, and λ 2698. The rays were then transmitted to λ 2625.

The three vapour bands were well marked, and the middle one stronger than the other two.

2-Dimethylpiperazine, C₆H₁₄N₂.

<i>t</i> °.	Pressure in mm.	
145	765	There were three diffuse bands at λ 2695— λ 2690, λ 2638— λ 2635, λ 2584— λ 2581, and the rays were then transmitted to λ 2490. The distance between the separate bands is about 55 units.
155	765	There were two bands at λ 2695— λ 2690 and λ 2638— λ 2635, and the rays were then transmitted to λ 2590.

3-Dimethylpiperazine, C₆H₁₄N₂.

130	765	There were three diffuse bands at λ 2748, λ 2688— λ 2684, λ 2634— λ 2630, and the rays were then transmitted to λ 2535.
140	765	There were three bands at λ 2741— λ 2739, λ 2690— λ 2685, λ 2634— λ 2630, and the rays were then transmitted to λ 2580. The distance between the separate bands is about 55 units.
150	765	The rays were absorbed between λ 2745— λ 2739, and λ 2688—2683, and then transmitted to λ 2660.

Each of the vapours of the two isomerides showed, therefore, three diffuse bands which are sharper on the more refrangible edges. They are also considerably wider apart than the vapour bands of piperazine, and the bands of the 3-compound are shifted more towards the red end than the corresponding ones of the 2-compound by about 50 units. The instability of the dibenzoyl derivatives made it difficult to take exact observations of the absorption of their vapours, but at the lower temperatures of observation no bands corresponding with the piperazine bands were observed. In the case of 1:4-dibenzoyl-3-dimethylpiperazine (m. p. 153°) at 170° the rays were transmitted to λ 2200. At 190° they were transmitted to λ 2270. In connexion with piperazine and its compounds it is of some interest to recall that the author (T., 1910, **97**, 1648) found four weak bands in the vapour of pyrrole, whereas neither solutions nor thin films of the substance exhibited any bands.

General Results.

The results of the preceding observations show that solutions of 2-dipyridyl possess a weak pyridine band, whereas 4-phenylpyridine has a strong one; that neutral solutions of piperidine show no bands, whereas acid solutions show a weak potential band, which covers the region of the vapour bands of piperidine described by the author (*loc. cit.*); that neutral solutions of 4-phenylpiperidine possess four weak bands, probably the residues of four benzene

solution bands, whereas acid solutions exhibit these four bands more feebly, and they also show strong indications of a weak pyridine band on the less refrangible side; that neutral solutions of benzoylpiperidine have no bands, whereas nitrosopiperidine has a large band, most likely connected with the nitroso-group; that piperazine and its derivatives have no bands, and are very transparent even in the strongest solutions.

As regards the vapours, those of 2-dipyridyl and 4-phenylpyridine show bands comparable with the solution bands. On the other hand, the vapours of 3:5-dichloropyridine and 2:3:5-trichloropyridine have a considerable number of narrow bands on the less refrangible edge of the pyridine band, and these narrow bands are completely absent from the solutions (*loc. cit.*). Also the vapours of 3:4:5-trichloropyridine, and the other pyridine derivatives investigated before, show no narrow bands, but only bands which are comparable with the strong solution bands (*loc. cit.*). Furthermore, the vapours of 4-phenylpiperidine, nitrosopiperidine, and benzoylpiperidine show none of the characteristic vapour bands of either piperidine or benzene. The vapour of piperine has one large band comparable with the solution band; the piperazine and its derivatives show three weak bands each. The latter are also interesting by reason of their great transparency; and, in this respect, they are like solutions of piperidine and pyrrole (*loc. cit.*).

An increase in the number of chlorine atoms in the pyridine nucleus is accompanied by a decrease in the number of narrow vapour bands, but the spatial position of the atoms is also a factor; for, although 2:3:5-trichloropyridine vapour exhibits a considerable number of such bands, the isomeric 3:4:5-trichloropyridine vapour has none. Similar results have been found by the author in the chloro- and bromo-derivatives of benzene and toluene (T., 1911, **99**, 811, 1699). This destruction of the narrow bands also occurs in the duplicated molecule 2-dipyridyl; and the author has shown that the vapour of naphthalene, a condensed benzene molecule, and the vapour of quinoline, a condensed benzene and pyridine molecule, show none of the narrow bands found in the vapours of benzene and pyridine (T., 1910, **97**, 1035; 1912, **101**, 1315).

With regard to 4-phenylpiperidine, the appearance of the four weak benzene bands in neutral solution, and of an additional weak pyridine band in the acid solution, together with the absence of the four bands in 4-phenylpyridine, would seem to lend some support to the conclusion of Dobbie and Fox (*loc. cit.*) that substances the molecules of which are composed of two nuclei will give the characteristic bands of the unsaturated one. This is only

partly true, even on the assumption that the four weak solution bands of 4-phenylpiperidine are the residues of the well-known seven solution bands of benzene. It is not true at all of the vapours of the substance, for not one of the numerous vapour bands of benzene or pyridine were observed.

That the varying valency of the nitrogen atom is of fundamental importance follows from the fact that the acid solutions of piperidine and 4-phenylpiperidine show indications of the large pyridine band which are absent from the neutral solution; but investigations with the isomerides of 4-phenylpyridine and 4-phenylpiperidine are necessary before a full discussion can be submitted.

It is established from these and earlier investigations that where a vibrating vapour molecule exhibits a series of narrow bands, such bands wholly disappear when the substance is in solution, and the solvent must therefore exercise an outstanding influence. The author has suggested before that the radiant energy of the source of light acting on the various atoms and groups of atoms in a molecule initiates the vibrations which produce selective absorption, and that the interactions of the different oscillatory centres, which may be centres of electronic vibrations, are modified by the type of nucleus as in benzene and pyridine; by the type and number of the side-chains as in the various derivatives of benzene and pyridine; by their physical condition as in the vapours at different temperatures and pressures; and by the solvent which absorbs a part of the radiant energy, whereby new interacting centres of oscillation are set in motion, and compensating effects take place, and damping and resisting forces brought into action.

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Xanthoxylum brachyacanthum, alkaloids
 of (JOWETT and PYMAN), T., 290 ; P.,
 26.
o-**Xylenes**, nitro-, oxidation of (WAR-
 NER), P., 60.
Xylenols, bromo- (CROSSLEY and
 RENOUF), P., 369.

Z.

Zinc, volatility of (NAIR and TURNER),
 T., 1534 ; P., 151.
 estimation of (FINLAY and CUMMING),
 T., 1004 ; P., 153.

FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

C_1 Group.

- CH₄** Methane, preparation and analysis of (CAMPBELL and PARKER), T., 1292 ; P., 130.
- CO** Carbon monoxide, properties of (MERRIMAN), P., 33.
- CO₂** Carbon dioxide, solubility of, in water (FINDLAY and WILLIAMS), T., 636 ; P., 115 ; influence of colloids and of suspensions of charcoal on the evolution of (FINDLAY and KING), T., 1170 ; P., 173.
- CN** Cyanogen, constitution of (DIXON and TAYLOR), T., 974 ; P., 113.

1 II

- CHN** Hydrocyanic acid, lead salt (GUPTA), P., 361.
- CHCl₃** Chloroform, latent heats of, and benzene, and of their mixtures (FLETCHER and TYRER), T., 517.
- CHI₃** Iodoform, preparation of (CHATTAWAY and BAXTER), T., 1987.
- CH₂O₂** Formic acid, preparation of (CHATTAWAY), P., 383 ; sodium salt, reduction of mercuric chloride by (FINDLAY and DAVIES), T., 1550 ; P., 250.
- CH₂N₂** Cyanamide, polymerisation of (MORRELL and BURGESS), P., 300.
- CH₃O** Methyl alcohol, solubility of alkali haloids in (TURNER and BISSETT), T., 1904 ; P., 263.
- CH₃N** Methylamine, platini-iodide of (DATTA), T., 427 ; P., 79.
- CH₅N₃** Guanidine, nitrite of, and its decomposition by heat (RÂY, DEY, and JANÂ), P., 283 ; thiocyanate of, formation of, from ammonium thiocyanate (KRALL), T., 1378 ; P., 189.
- CO₈N₄** Tetranitromethane, colour reactions of, with various substances (HARPER and MACBETH), P., 304 ; colour reactions of, with compounds containing elements of varying valency (CLARKE, MACBETH, and STEWART), P., 161.
- CNBr** Cyanogen bromide, reactions of (DIXON and TAYLOR), T., 974 ; P., 113.

1 III

- CHON** Cyanic acid, polymerisation of (WERNER), T., 1010 ; P., 132 ; ammonium salt, transformation of, into carbamide (WERNER), T., 1010 ; P., 132.

- CHNS** Thiocyanic acid, ammonium salt, formation of guanidine thiocyanate from (KRALL), T., 1378 ; P., 189.
- CH₄ON₂** Carbamide, transformation of ammonium cyanate into, and its decomposition by heat (WERNER), T., 1010 ; P., 132 ; decomposition of (BURROWS and FAWSITT), P., 264 ; decomposition of, by heat (WERNER), T., 2275 ; P., 287 ; condensation of chloral hydrate and (COPPIN and TITHERLEY), P., 352.
- CH₄N₂S** Thiocarbamide, action of, with iodine (MARSHALL), P., 14 ; action of nitrous acid with (COADE and WERNER), T., 1221 ; P., 188.
- CH₃ON₃** Semicarbazide, action of the hydrochloride of, on *p*-quinones (HEILBRON and HENDERSON), T., 1404 ; P., 226.

C₂ Group.

- C₂H₂O₂** Glyoxal, action of magnesium aryl haloids on (WREN and STILL), T., 1770 ; P., 262.
- C₂H₂O₄** Oxalic acid, interaction of, with glycerol (CHATTAWAY), P., 383 ; neutral and acid potassium salts of (HARTLEY, DRUGMAN, VLIELAND, and BOURDIL-
LON), 1747 ; P., 252.
- C₂H₃O₂** Acetic acid, ammonium salt, vapour density of (RÂV and JÂNÂ), T., 1565 ; P., 234.
- C₂H₅N** Ethylamine, platini-iodide of (DATTA), T., 428 ; P., 79.
- C₂H₆O** Ethyl alcohol, densities of mixtures of ethyl acetate and (MERRIMAN), T., 1774 ; P., 259 ; azeotropic mixtures of ethyl acetate, water, and (MERRIMAN), T., 1790, 1801 ; P., 259, 260 ; vapour pressure of, and of its azeotropic mixtures with water (MERRIMAN), T., 628 ; P., 68 ; equilibrium of, with xylene and water (HOLT and BELL), P., 383 ; solubility of alkali haloids in (TURNER and BISSETT), T., 1904 ; P., 263.
- C₂H₇N** Dimethylamine, platini-iodide of (DATTA), T., 428 ; P., 79.

2 III

- C₂H₃O₂Cl₃** Chloral hydrate, condensation of carbamide with (COPPIN and TITH-
ERLEY), P., 352.
- C₂H₃O₂Br** Bromoacetic acid, action of alkalis in methyl-alcoholic solution on (MADSEN), T., 965 ; P., 129.
- C₂H₅O₂N₃** Biuret, action of heat on (WERNER), T., 2275 ; P., 287.

2 IV

- C₂H₂O₂NK** Potassium diformamide (RAKSHIT), T., 1559 ; P., 195.
- C₂H₂O₂NNa** Sodium diformamide (RAKSHIT), T., 1557 ; P., 195.
- C₂H₄ONK** Potassium acetamide (RAKSHIT), T., 1560 ; P., 195.

C₃ Group.

- C₃H₃O₃** Pyruvic acid, condensation of aromatic aldehydes with (LUBRZYNSKA and SMEDLEY), P., 174.
- C₃H₅O₃** Acid, from phytin (CLARKE), P., 27.
- C₃H₆O** Allyl alcohol, preparation of (CHATTAWAY), P., 383.
Acetone, purification of, with sodium iodide (SHIPSEY and WERNER), T., 1255 ; P., 194 ; crystallisation of sodium iodide with (SHIPSEY and WERNER), P., 117 ; condensation of, with glucose (MACDONALD), T., 1896 ; P., 260.
- C₃H₆N₄** *iso*Melamine (KRALL), P., 377.
- C₃H₇N** Allylamine, platini-iodide of (DATTA), T., 428 ; P., 79 ; allyl oxamate, hydrogen oxalate and oxalate of (GLUUD), T., 945.

- C_3H_8O Propyl alcohol, solubility of alkali haloids in (TURNER and BISSETT), T., 1904; P., 263.
 $C_3H_8O_3$ Glycerol, interaction of, with oxalic acid (CHATTAWAY), P., 383.
 C_3H_9N Trimethylamine, platini-iodide of (DATTA), T., 429; P., 79.

3 III

- $C_3H_4O_2N_4$ Ammelide, preparation of (WERNER), T., 2275; P., 287.
 $C_3H_5O_2Br$ α -Bromopropionic acid, action of alkalis in methyl-alcoholic solution on (MADSEN), T., 965; P., 129.
 $C_3H_5O_3N_3$ Glyceryl trinitrate, partial pressure of, in acetone solution (MARSHALL), P., 157.

3 IV

- $C_3H_3ON_2Cl_3$ β -Trichloroethylidenecarbamide (COPPIN and TITHERLEY), P., 353.
 $C_3H_5O_2N_2Cl_3$ β -Trichloro- α -hydroxyethylcarbamide (COPPIN and TITHERLEY), P., 352.
 C_3H_6ONK Potassium propionamide (RAKSHIT), T., 1560.

C₄ Group.

- $C_4H_4O_4$ Malic anhydride (DENHAM and WOODHOUSE), T., 1870; P., 262.
 $C_4H_6O_3$ Acetic anhydride, rate of hydration of (WILSDON and SIDGWICK), T., 1959; P., 265.
 $C_4H_6O_4$ Succinic acid, optical rotatory power of derivatives of (CLOUGH), P., 352.
 $C_4H_6O_5$ Glycollic anhydride (DENHAM and WOODHOUSE), T., 1869.
 Malic acid, cupric salt (PICKERING), T., 1354; P., 191; ferric salt (PICKERING), T., 1361; P., 191.
 $C_4H_6O_6$ Tartaric acid, rotation of, and of its derivatives (CLOUGH), P., 352; action of, on tin, in presence of oxygen (CHAPMAN), T., 775; P., 122; ferric salt (PICKERING), T., 1362; P., 191.
 $C_4H_8O_2$ Ethyl acetate, azeotropic mixtures of ethyl alcohol, water, and (MERRIMAN), T., 1790, 1801; P., 259, 260; mutual solubilities of water and, and the densities of its mixtures with ethyl alcohol (MERRIMAN), T., 1774; P., 259.
 $C_4H_8O_3$ Methyl *l*-lactate, rotation of (PATTERSON and FORSYTH), T., 2266.
 $C_4H_8Br_2$ $\alpha\gamma$ -Dibromobutane, action of, on the sodium derivative of diethyl malonate (BLACKSTOCK and PERKIN), P., 74; action of, on the sodium derivatives of ethyl acetoacetate and benzoylacetate (FARGHER and PERKIN), P., 72.
 $C_4H_{10}O$ Methyleneethylcarbinol, resolution of, and its salts (PICKARD and KENYON), T., 1941.
 $C_4H_{10}N_2$ Hexahydropyrimidine or methylene- $\alpha\gamma$ -diaminopropane, and its salts (TITHERLEY and BRANCH), T., 334; P., 29.
 Piperazine, absorption spectra of (PURVIS), T., 2286.
 $C_4H_{11}N$ Diethylamine, platini-iodide of (DATTA), T., 428; P., 79.

4 III

- $C_4H_5O_4Br$ Bromosuccinic acid, action of alkalis in methyl-alcoholic solution on (MADSEN), T., 965; P., 129.
 $C_4H_6O_3N_4$ Allantoin, constitution of (TITHERLEY), T., 1336; P., 109.
 $C_4H_6O_3S$ Thionyl derivative of glycollic acid (DENHAM and WOODHOUSE), T., 1869.
 C_4H_7ON Allylformamide, preparation of (GLUUD), T., 941.
 $C_4H_9ON_3$ Nitrosopiperazine, nitrite of (RAY and RAKSHIT), T., 1.
 $C_4H_{13}ON$ Tetramethylammonium hydroxide, platini-iodide of (DATTA), T., 429; P., 79.

4 IV

$C_4H_4O_4Cl_2S_2$ Anhydride, from sulphur chloride and silver monochloroacetate (DENHAM and WOODHOUSE), T., 1866.

C₅ Group.

- C_5H_5N Pyridine, cupri- and platini-iodides of (DATTA), T., 429 ; P., 79.
 $C_5H_6O_5$ Acetonedicarboxylic acid, condensation of, with phenols (DEV), P., 154.
 $C_5H_7N_5$ 4-Triazo-3-5-dimethylpyrazole (MORGAN and REILLY), P., 379.
 $C_5H_8O_2$ Acetylacetone, influence of, on ionic reactions (HEWITT and MANN), P., 30 ; caesium, lithium, and scandium salts (MORGAN and MOSS), P., 373.
 $C_5H_9N_3$ 4-Amino-3-5-dimethylpyrazole, salts of (MORGAN and REILLY), P., 379.
 $C_5H_{10}O_3$ Methyl *l*- α -methoxypropionate, rotation of (PATTERSON and FORSYTH), T., 2268.
 $C_5H_{10}O_4$ Methyl tetrose (GILMOUR), P., 108, 363.
 $C_5H_{10}O_5$ Methyl tetronic acid, brucine salt of (GILMOUR), P., 363.
 $C_5H_{10}Br_2$ α -Dibromopentane (CLARKE), T., 1703.
 $C_5H_{11}N$ Piperidine, absorption spectra of (PURVIS), T., 2285.
 $C_5H_{11}Cl$ *d*-Amyl chloride (McKENZIE and CLOUGH), T., 699.
 $C_5H_{12}O$ *iso*Amyl alcohol, solubility of alkali haloids in (TURNER and BISSETT), T., 1904 ; P., 263.
 C_5NCl_5 Pentachloropyridine, absorption spectra of (PURVIS), T., 2291.

5 III

- C_5HNCl_4 2:3:4:5-Tetrachloropyridine, absorption spectra of (PURVIS), T., 2291.
 $C_5H_2NCl_3$ Trichloropyridines, absorption spectra of (PURVIS), T., 2289.
 $C_5H_2N_2Cl_4$ Tetrachloro-2-aminopyridine, absorption spectra of (PURVIS), T., 2291.
 $C_5H_2NCl_2$ 3:5-Dichloropyridine, absorption spectra of (PURVIS), T., 2288.
 $C_5H_7O_2N$ Ethyl cyanoacetate, condensation of, with acid chlorides (WEIZMANN, STEPHEN, and AGASHE), T., 1855 ; P., 261.
 $C_5H_7O_3N$ Allyloxamic acid, and its salts (GLUUD), T., 943.
 $C_5H_9O_2N$ Proline, detection of (GLUUD), P., 177.
 Allylglycine, copper salt (GLUUD), P., 177.
 $C_5H_9O_3N$ γ -Oximino- α -ethoxyacetone (WEIZMANN, STEPHEN, and AGASHE), T., 1857.
 $C_5H_{10}O_2N$ Nitrosopiperidine, absorption spectra of (PURVIS), T., 2285.

5 IV

- $C_5H_5O_3N_2Cl_6$ Di-(β -trichloro- α -hydroxyethyl)carbamide (COPPIN and TITHERLEY), P., 352.
 $C_5H_{11}O_2ClS$ *d*-Amyl chlorosulphinate (McKENZIE and CLOUGH), T., 698.

C₆ Group.

- C_6H_6 Benzene, absorption spectra of derivatives of (PURVIS and McCLELAND), T., 1088 ; P., 132 ; absorption spectra of derivatives of, containing sulphur (FOX and POPE), T., 1263 ; P., 194 ; and chloroform, latent heats of, and of their mixtures (FLETCHER and TYRER), T., 517.

6 II

- $C_6H_4O_2$ Quinol, cause of the blue fluorescence developing in solutions containing alkali sulphites and (PORTER), P., 4.

- $C_6H_4O_6$ Sarsapic acid (POWER and SALWAY), P., 372.
- C_6H_6O Phenol, absorption spectra of derivatives of (PURVIS), T., 1638 ; P., 253 ; oxidation of, by bacteria (FOWLER and MUMFORD), P., 156.
- $C_6H_6N_2$ Phenyl-di-imine, nature of Vaubel's supposed (FORSTER and WITHERS), T., 266 ; P., 24.
- C_6H_7N Aniline, absorption spectra of derivatives of (PURVIS), T., 1638 ; P., 253 ; platin-iodide of (DATTA), T., 428 ; P., 79.
- $C_6H_5O_7$ Citric acid, cupric salt (PICKERING), T., 1354 ; P., 191 ; ferric salt (PICKERING), T., 1362 ; P., 191.
- $C_6H_8N_2$ *p*-Phenylenediamine, influence of substitution on the reactivity of (MORGAN and PICKARD), P., 229.
- $C_6H_9O_4$ Methyl-*l*- α -acetoxypropionate rotation of (PATTERSON and FORSYTH), T., 2267.
- $C_6H_{10}O_2$ 1-Methylcyclobutane-2-carboxylic acid (BLACKSTOCK and PERKIN), P., 74.
- $C_6H_{10}O_3$ Ethyl acetoacetate, condensation of, with acid chlorides (WEIZMANN, STEPHEN, and AGASHE), T., 1855 ; P., 261.
- Propionic anhydride, rate of hydration of (WILSDON and SIDGWICK), T., 1959 ; P., 265.
- $C_6H_{10}O_4$ Ethylene glycol diacetate, hydrolysis of (BAINBRIDGE), P., 4.
- $C_6H_{12}O_8$ Dextrose, condensation of, with acetone (MACDONALD), T., 1896 ; P., 260.
- d*-Mannose, formation of, from *d*-glucosamine (IRVINE and HYND), P., 306.
- $C_6H_{12}O_7$ Gluconic acid, ammonium salt (IRVINE, THOMSON, and GARRETT), T., 245 ; P., 7.
- $C_6H_{14}O$ Ethyl-*n*-propylcarbinol, resolution of, and its salts (PICKARD and KENYON), T., 1942.
- $C_6H_{14}O_6$ Dulcitol, melting point of (FURLONG and CAMPBELL), P., 128.
- $C_6H_{14}N_2$ 2- and 3-Dimethylpiperazines, absorption spectra of (PURVIS), T., 2287.
- cis*-2:6-Dimethylpiperazine (POPE and READ), P., 382.
- $C_6H_{15}N$ Triethylamine platin-iodide (DATTA), T., 429 ; P., 79.
- Dimethylbutylamine and its pierate (CLARKE), T., 1696.

6 III

- C_6HNCI_6 2:3:4-Hexachloropicoline, absorption spectra of (PURVIS), T., 2292.
- $C_6H_2O_6N_4$ 4:6-Dinitrobenz*iso*oxadiazole oxide (GREEN and ROWE), T., 2029 ; P., 276.
- $C_6H_3O_6N_3$ 6-Nitrobenz*iso*oxadiazole oxide (GREEN and ROWE), T., 2028 ; P., 276.
- $C_6H_3O_6N_3$ Trinitrobenzene, absorption spectra of (BALY and RICE), T., 2085 ; P., 216.
- $C_6H_3O_7N_3$ Picric acid, absorption spectra of (BALY and RICE), T., 2085 ; P., 216.
- $C_6H_4O_6N_4$ 2:4:6-Trinitroaniline (*picramide*), potassium salt (GREEN and ROWE), T., 513.
- $C_6H_4O_7N_4$ Trinitro-*p*-aminophenols, constitution of (MELDOLA and REVERDIN), T., 1484 ; P., 248.
- C_6H_5ONa Sodium phenoxide, relative activities of alkyl iodides with (SEGALLER), T., 1154, 1421 ; P., 159, 246, 305, 379.
- C_6H_5ON Nitrobenzene, solubility of polybromides in (JOSEPH), T., 1554 ; P., 72.
- $C_6H_4O_4N_3$ 2:4-Dinitroaniline, potassium salt of (GREEN and ROWE), T., 513.
- $C_6H_5O_2N_2$ *o*- and *p*-Nitroanilines, sodium salts of (GREEN and ROWE), T., 511.

- C_6H_6NI *m*-Iodoaniline, hydrochloride of (McCOMBIE and WARD), T., 1999
p-Iodoaniline, preparation of derivatives of (CHATTAWAY and CONSTABLE), P., 304.
- $C_6H_9O_3Na$ Ethyl sodioacetoacetate, action of $\alpha\gamma$ -dibromobutane on (FARGHER and PERKIN), P., 72.
- $C_6H_9O_4N$ Fructoseazine (IRVINE, THOMSON, and GARRETT), T., 247.
- $C_6H_{12}O_4N_2$ $\alpha\delta$ -Diaminoadipic acid, and its copper salt (STEPHEN and WEIZMANN), T., 274.
- $C_6H_{13}OBr$ Methyl ϵ -bromoamyl ether (CLARKE), T., 1703.
- $C_6H_{13}O_5N$ *d*-Glucosamine, conversion of, into *d*-mannose (IRVINE and HYND), P., 306.
- $C_6H_{15}ON$ Methyl γ -dimethylaminopropyl ether, and its picrate (CLARKE), T., 1702.
- $C_6H_{15}O_8P$ β -Diglycerolphosphoric acid, calcium salt, true nature of the so-called (TUTIN), P., 228.
- $C_6O_2Cl_3I$ 2:3:6-Trichloro-5-iodo-*p*-benzoquinone (McCOMBIE and WARD), T., 2003.

6 IV

- C_6HOCl_4Br 2:3:4:6-Tetrachloro-5-bromophenol (McCOMBIE and WARD), T., 2005.
- C_6HOCl_4I 2:3:4:6-Tetrachloro-5-iodophenol (McCOMBIE and WARD), T., 2004.
- C_6HOCl_5Br 2:2:3:4:4:6-Hexachloro-5-bromo- Δ^5 -cyclohexenone (McCOMBIE and WARD), T., 2004.
- C_6HOCl_5I 2:2:3:4:4:6-Hexachloro-5-iodo- Δ^5 -cyclohexenone (McCOMBIE and WARD), T., 2002; P., 283.
- $C_6H_2OCl_3Br$ 2:4:6-Trichloro-3-bromophenol (McCOMBIE and WARD), T., 2005.
- $C_6H_2OCl_3I$ 2:4:6-Trichloro-3-iodophenol (McCOMBIE and WARD), T., 2003.
- $C_6H_3ON_2Cl$ Chlorobenzisooxadiazole (*chlorobenzfurozan*) (GREEN and ROWE), T., 900.
- $C_6H_3ON_2Cl_3$ 2:3:4-Trichloropicolinamide, absorption spectra of (PURVIS), T., 2292.
- $C_6H_3ON_2Br$ 4-Bromobenzisooxadiazole (FORSTER and BARKER), T., 1923.
- $C_6H_3OCl_2$ 6-Chloro-2:4-di-iodophenol (KING and McCOMBIE), T., 229; P., 8.
- $C_6H_3OBr_2I$ 2:6-Dibromo-4-iodophenol (KING and McCOMBIE), T., 227; P., 8.
- $C_6H_3O_2N_2Cl$ Chlorobenzisooxadiazole oxide (*chlorobenzfuroxan*) (GREEN and ROWE), T., 899.
- $C_6H_3O_2N_2Br$ 4-Bromobenzisooxadiazole oxide (FORSTER and BARKER), T., 1921.
- $C_6H_3O_2N_4Br$ 4- and 5-Bromo-2-nitrophenylazoimides (FORSTER and BARKER), T., 1920.
- $C_6H_3NCl_3I$ 2:4:6-Trichloro-3-iodoaniline (McCOMBIE and WARD), T., 2000; P., 283.
- C_6H_4OBrI 2-Bromo-4-iodophenol (KING and McCOMBIE), T., 231; P., 8.
- $C_6H_5O_2N_2Cl$ Chloro-*o*-benzoquinonedioxime (GREEN and ROWE), T., 900.
- $C_6H_5O_3N_2Br$ Bromonitro-*p*-aminophenol (MELDOLA and HOLLELY), T., 183.
- $C_6H_7O_3NS$ Aniline-*p*-sulphonic acid (*sulphanilic acid*), and its hydrates, solubility of (PHILIP), T., 284; P., 28.
- $C_6H_{10}O_2NNa$ Sodium dipropionamide (RAKSHIT), T., 1560.
- $C_6H_{12}ONBr$ α -Ethylbutyrobromoamide (PYMAN), T., 858.

6 V

- $C_6H_2OCl_2BrI$ 6-Chloro-2-bromo-4-iodophenol (KING and McCOMBIE), T., 232; P., 8.

$C_6H_3OCl_2Br_2I$ 2:6-Dibromo-4-iodophenol dichloride (KING and McCOMBIE), T., 227; P., 8.

C₇ Group.

C_7H_6O Benzaldehyde, absorption spectra of derivatives of (PURVIS), T., 1638; P., 253.

$C_7H_6O_2$ Benzoic acid, ammonium salt, vapour density of (RÂY and JÂNÂ), T., 1565; P., 234.

$C_7H_8O_4$ β -Methylmuconic acid (STEPHEN and WEIZMANN), T., 276; P., 14.

$C_7H_{10}O_2$ 1-Methyldihydroresorcin, and its silver salt (GILLING), T., 2032; P., 286.

$C_7H_{10}O_3$ *cyclo*Hexanone-4-carboxylic acid, and the optically active salts of its derivatives (MILLS and BAIN), P., 309.

$C_7H_{10}O_4$ $\alpha\gamma$ -Dimethylglutaconic acid, labile (THORPE and WOOD), T., 279; P., 5.

1-Methyl*cyclobutane*-2:2-dicarboxylic acid (BLACKSTOCK and PERKIN), P., 74.

$C_7H_{10}O_6$ *iso*Butane- $\alpha\gamma\gamma'$ -tricarboxylic acid (THORPE and WOOD), T., 1581; P., 255.

$C_7H_{12}O_2$ Heptane- $\beta\zeta$ -dione (FARGHER and PERKIN), P., 73.

$C_7H_{12}O_4$ Diethyl malonate, condensation of, with acid chlorides (WEIZMANN, STEPHEN, and AGASHE), T., 1855; P., 261; sodium derivatives of, and their absorption spectra (MACBETH and STEWART), P., 11.

$\alpha\beta$ -Dimethoxyvalerolactone (GILMOUR), P., 363.

$C_7H_{12}O_5$ Substance, from methylation of cellulose (DENHAM and WOODHOUSE), T., 1739; P., 251.

$C_7H_{14}O$ 2:6-Dimethyl-2:3:5:6-tetrahydro-1:4-pyran (FARGHER and PERKIN), P., 73.

$C_7H_{14}O_2$ Heptan- ζ -ol- β -one (FARGHER and PERKIN), P., 73.

$C_7H_{14}O_6$ Monomethyl glucoses (IRVINE and SCOTT), T., 571; P., 70.

$C_7H_{14}Br_2$ $\beta\zeta$ -Dibromoheptane (FARGHER and PERKIN), P., 73.

$C_7H_{16}O$ Ethyl-*m*-butylcarbinol, resolution of, and its salts (PICKARD and KENYON), T., 1943.

$C_7H_{17}N$ δ -Aminoheptane, platinichloride of (PYMAN), T., 859.

Dimethyl-*n*- and *iso*-amylamines, and their picrates (CLARKE), T., 1697.

7 III

$C_7H_5OCl_5$ 2:4:4:5-Pentachloro-3-methyl- $\Delta^{2:5}$ -*cyclo*hexadienone (CROWTHER and McCOMBIE), T., 547; P., 69.

$C_7H_5O_2Cl_3$ 2:4:5-Trichlorotoluquinone, preparation of (CROWTHER and McCOMBIE), T., 548; P., 69.

$C_7H_4OCl_4$ 2:4:5:6-Tetrachloro-*m*-cresol (CROWTHER and McCOMBIE), T., 546; P., 69.

$C_7H_5OCl_3$ 2:4:6-Trichloro-*m*-cresol (CROWTHER and McCOMBIE), T., 545; P., 69.

$C_7H_5O_2Cl$ *m*-Chlorobenzoic acid, preparation of, and its hydroxylamine salt (GLUUD and KEMPF), T., 1530; P., 244.

$C_7H_5O_7N_3$ Trinitroanisole, absorption spectra of (BALY and RICE), T., 2085; P., 216.

$C_7H_6O_3N_2$ 5-Methylbenzisooxadiazole oxide (*tolufurazan oxide*, *tolufuroxan*, *dinitrosotoluene*, *o-toluquinonedioximeperoxide*), preparation of (GREEN and ROWE), T., 898.

$C_7H_6O_2N_4$ Nitrotriazotoluenes (FORSTER and BARKER), T., 1921.

$C_7H_6O_2N_2$ *o*-, *m*-, and *p*-Nitrobenzaldoximes, *syn*- and *anti*-forms of (BRADY and DUNN), T., 1619; P., 248.

- $C_7H_6O_6N_2$ 4:6-Dinitroguaiacol, and its barium salt (MELDOLA and REVERDIN), T., 1488.
- $C_7H_6O_7N_4$ Trinitro-*p*-anisidines, constitution of (MELDOLA and REVERDIN), T., 1484; P., 248.
- $C_7H_7O_2N_3$ 4-Hydroxybenzeneazoformamide, and its salts (HEILBRON and HENDERSON), T., 1414.
- $C_7H_8O_2N_2$ *m*-Nitro-*p*-toluidine, sodium salt (GREEN and ROWE), T., 512.
- $C_7H_8O_5N_4$ 3:5-Dinitro-2:4-diaminoanisole (MELDOLA and REVERDIN), T., 1490.
- $C_7H_9O_2N_3$ 4-Nitro-2:5-tolylenediamine (MORGAN and MICKLETHWAIT), T., 1378.
- $C_7H_{10}O_4Br_2$ $\alpha\delta$ -Dibromo- β -methyladipic acid (STEPHEN and WEIZMANN), T., 272.
- $C_7H_{11}O_3N$ Ethyl allyloxamate (GLUUD), T., 943.
- $C_7H_{11}O_4Na$ Diethyl sodiomalonate, action of $\alpha\gamma$ -dibromobutane on (BLACK-STOCK and PERKIN), P., 74.
- $C_7H_{13}ON$ ϵ -Methoxyhexonitrile (CLARKE), T., 1704.
- $C_7H_{13}ON_3$ α - and β -Semicarbazones of mesityl oxide (WILSON and HEILBRON), T., 377; P., 59.
- $C_7H_{13}OBr$ ζ -Bromoheptan- β -one (FARGHER and PERKIN), P., 73.
- $C_7H_{17}ON$ Methyl δ -dimethylaminobutyl ether, and its picrate (CLARKE), T., 1702.
- Methyl ζ -aminohexyl ether (CLARKE), T., 1704.

7 IV

- $C_7H_7O_2NCl_3$ Methyl 2:3:4-trichloropicolinate, absorption spectra of (PURVIS), T., 2291.
- $C_7H_5O_2N_3Cl_2$ 3:5-Dichloro-4-hydroxybenzeneazoformamide (HEILBRON and HENDERSON), T., 1417.
- $C_7H_6O_2N_3Cl$ 3-Chloro-4-hydroxybenzeneazoformamide, and its sodium salt (HEILBRON and HENDERSON), T., 1416.
- $C_7H_9O_3NS$ Methylaniline- ω -sulphonic acid, sodium salt (POPE and WILLETT), T., 1259.

 C_8 Group.

- C_8H_{10} *o*-Xylene, derivatives of (CROSSLEY and PRATT), T., 982; P., 169; (CROSSLEY and SMITH), T., 989; P., 170; (SIMONSEN), T., 1144; P., 26, 126; (CROSSLEY and BARTLETT), T., 1297; P., 217; (CROSSLEY), T., 2179; P., 352.
- m*-Xylene, equilibrium of, with ethyl alcohol and water (HOLT and BELL), P., 383.
- C_8H_{12} 1:2-Dimethyl- $\Delta^{2,6}$ -cyclohexadiene (HAWORTH), T., 1246; P., 193.
- 1:3-Dimethyl- $\Delta^{1,3}$ -cyclohexadiene (HAWORTH), T., 1248.
- Cantharene, and allied hydrocarbons (HAWORTH), T., 1242; P., 193.

8 II

- $C_8H_8O_6$ Dimethyl sarsapate (POWER and SALWAY), P., 372.
- C_8H_9Cl *o*-Chloroethylbenzene, preparation and rotation of (MCKENZIE and CLOUGH), T., 694.
- $C_8H_{10}O$ Phenylmethylcarbinols, optically active, interconversion of (MCKENZIE and CLOUGH), T., 687; P., 109.
- $C_8H_{10}O_5$ Anhydro-acid from $\beta\beta$ -dimethylpropanetricarboxylic acid (THORPE and WOOD), T., 1584.
- $C_8H_{12}O_2$ Acetyl mesityl oxide, vanadium salt (MORGAN and MOSS), P., 374.
- Dimethyldihydroresorcin, bromoxilenols from (CROSSLEY and RENOUF), P., 369.
- dl*-1-Methyl- Δ^1 and - Δ^6 -cyclohexene-3-carboxylic acids, resolution of (HAWORTH and PERKIN), T., 2231, 2235.

- $C_8H_{12}O_5$ Hexan- ϵ -one- $\alpha\gamma$ -dicarboxylic acid (HAWORTH and PERKIN), T., 2231.
 $C_8H_{12}O_6$ $\beta\beta$ -Dimethylpropanetricarboxylic acid, and its silver salt (THORPE and WOOD), T., 1583; P., 255.
 $C_8H_{14}O$ 1:2-Dimethyl- Δ^6 -cyclohexen-2-ol (HAWORTH), T., 1247.
 $C_8H_{14}O_3$ Butyric anhydride, rate of hydration of (WILSDON and SIDGWICK), T., 1959; P., 265.
 $C_8H_{16}O_6$ $\beta\gamma$ -Dimethyl α - and β -glucoses (IRVINE and SCOTT), T., 583; P., 71.
 Monomethyl methylglucoside (IRVINE and SCOTT), T., 573; P., 71.
 $C_8H_{18}O$ Ethyl-*n*-amylcarbinol, resolution of (PICKARD and KENYON), T., 1944.
 $C_8H_{19}N$ Dimethyl-*n*- and -*iso*-hexylamines, and their picrates (CLARKE), T., 1697.

8 III

- $C_8H_4O_8N_2$ 3:4-Dinitro-*o*-phthalic acid (WARNER), P., 61.
 $C_8H_5O_2I_3$ 2:4:6-Tri-iodophenyl acetate dichloride (KING and McCOMBIE), T., 226.
 $C_8H_6O_6N_2$ 3:4-Dinitro-*o*-toluic acid (WARNER), P., 61.
 $C_8H_6O_8N_4$ 2:3:5-Trinitro-*p*-acetylaminophenol (MELDOLA and REVERDIN), T., 1493.
 C_8H_6NI *o*-Iodo-*p*-toluonitrile (KENNER and WITHAM), T., 235.
 $C_8H_7OCl_3$ 2:4:6-Trichloro-*m*-tolyl methyl ether (CROWTHER and McCOMBIE), T., 545.
 $C_8H_7O_5N$ *m*-Nitrophenoxyacetic acid (HEWITT, JOHNSON, and POPE), T., 1631.
 $C_8H_8OBr_2$ 4:5-Dibromo-3-*o*-xylenol (CROSSLEY and SMITH), T., 989; P., 170.
 $C_8H_8O_4N_2$ Dinitro-*o*-xylene (SIMONSEN), T., 1152.
 $C_8H_8O_6N_2$ 5:6-Dinitro-3-hydroxy-*o*-tolyl methyl ether (CAIN and SIMONSEN), P., 380.
 C_8H_9OBr 5-Bromo-*o*-3-xylene (CROSSLEY), T., 2181; P., 352.
 5- and 6-Bromo-*o*-4-xyleneols (CROSSLEY and BARTLETT), T., 1299; P., 217.
 $C_8H_9O_2N_3$ 4-Hydroxy-*m*-tolueneazofornamide, and its sodium salt (HEILBRON and HENDERSON), T., 1417.
 $C_8H_9O_3N$ 5-Nitro-*o*-3-xylene (CROSSLEY), T., 2181.
 $C_8H_{10}O_2N_2$ *p*-Nitroethylaniline, sodium salt of (GREEN and ROWE), T., 512.
 $C_8H_{10}NBr$ 6-Bromo-*o*-4-xylidine (CROSSLEY and BARTLETT), T., 1300.
 $C_8H_{11}ON$ 5-Amino-*o*-3-xylene (CROSSLEY), T., 2181.
 $C_8H_{12}O_2N_2$ Diallyloxamide, preparation of (GLUDD), T., 942.
 $C_8H_{12}O_4Br_2$ Methyl $\alpha\delta$ -dibromoadipate (STEPHEN and WEIZMANN), T., 271; P., 14.
 $C_8H_{14}O_4S_2$ Anhydride, from sulphur chloride and silver *n*-butyrate (DENHAM and WOODHOUSE), T., 1865.
 $C_8H_{15}ON$ δ -Carbimidoheptane (PYMAN), T., 860.
 $C_8H_{17}O_5N$ Dimethylaminoglucose (IRVINE, THOMSON, and GARRETT), T., 249; P., 7.
 Ethylaminoglucose (IRVINE, THOMSON, and GARRETT), T., 246; P., 7.
 α -Aminoethylglucoside, hydrochloride of (IRVINE and HYND), T., 53.
 $C_8H_{19}ON_2$ δ -Heptylcarbamide (PYMAN), T., 860.
 $C_8H_{19}ON$ Methyl ϵ -dimethylaminoamyl ether, and its picrate (CLARKE), T., 1703.
 $C_8H_{21}ON$ Tetraethylammonium hydroxide, cupri- and platini-iodides of (DATTA), T., 429; P., 70.

8 IV

- $C_8H_3O_2Cl_4Br$ Acetyl derivative of 2:3:4:6-tetrachloro-5-bromophenol (McCOMBIE and WARD), T., 2005.
- $C_8H_3O_2Cl_4I$ Acetyl derivative of 2:3:4:6-tetrachloro-5-iodophenol (McCOMBIE and WARD), T., 2004.
- $C_8H_4O_2Cl_3Br$ Acetyl derivative of 2:4:6-trichloro-3-bromophenol (McCOMBIE and WARD), T., 2005.
- $C_8H_4O_2Cl_3I$ Acetyl derivative of 2:4:6-trichloro-3-iodophenol (McCOMBIE and WARD), T., 2003.
- $C_8H_5O_2ClI$ 6-Chloro-2:4-di-iodophenyl acetate (KING and (McCOMBIE), T., 230.
- $C_8H_5O_2Cl_2I$ 6-Chloro-2:4-di-iodophenyl acetate dichloride (KING and McCOMBIE), T., 230.
- $C_8H_5O_2Br_2I$ 2:6-Dibromo-4-iodophenyl acetate (KING and McCOMBIE), T., 228.
- $C_8H_6O_2Cl_2I_2$ 2:4-Di-iodophenyl acetate dichloride (KING and McCOMBIE), T., 229.
- $C_8H_6O_2BrI$ 2-Bromo-4-iodophenyl acetate (KING and McCOMBIE), T., 281.
- C_8H_8ONI *o*-Iodo-*p*-toluamide (KENNER and WITHAM), T., 236.
- $C_8H_8O_2NBr$ 3-Bromo-5-nitro-*o*-xylene (CROSSLEY and BARTLETT), T., 1300.
- $C_8H_8O_2N_3Br$ 5-Bromo-4-hydroxy-*m*-tolueneazoformamide (HEILBRON and HENDERSON), T., 1418.
- $C_8H_9ON_2I$ *o*-Iodo-*p*-toluhydrazide (KENNER and WITHAM), T., 236.
- $C_8H_9O_5NS$ 3-Nitro-*o*-xylene-4- and -5-sulphonic acids, and their barium salts (SIMONSEN), T., 1146; P., 126.
- 4-Nitro-*o*-xylene-5-sulphonic acid (SIMONSEN), T., 1149; P., 26, 126.
- $C_8H_{10}O_3NCl$ Ethyl β -chloropropionylcyanoacetate, and its copper compound (WEIZMANN, STEPHEN, and AGASHE), T., 1857.
- $C_8H_{10}O_4N_2S$ 3-Nitro-*o*-xylene-4- and -5-sulphonamides (SIMONSEN), T., 1146.
- 4-Nitro-*o*-xylene-5-sulphonamide (SIMONSEN), T., 1149.
- $C_8H_{11}O_3NS$ 3-*o*-Xylidine 4-sulphonic acid (+ H_2O), and its barium salt (SIMONSEN), T., 1149; P., 126.
- o*-3- and -4-Xylidine-5-sulphonic acids (+ H_2O), and their barium salts (SIMONSEN), T., 1147; P., 126.
- o*-3- and -4-Xylidine-6-sulphonic acids, and their barium salts (SIMONSEN), T., 1150; P., 126.
- $C_8H_{16}ONBr$ α -Propylvalerobromoamide (PYMAN), T., 857.

8 V

- $C_8H_5ONCl_3I$ 2:4:6-Trichloro-3-iodoacetanilide (McCOMBIE and WARD), T., 1999.
- $C_8H_5O_2Cl_2Br_2I$ 2:6-Dibromo-4-iodophenyl acetate dichloride (KING and McCOMBIE), T., 228.
- $C_8H_6O_2Cl_2BrI$ 2-Bromo-4-iodophenyl acetate dichloride (KING and McCOMBIE), T., 231.
- $C_8H_5O_4NSCl$ 3-Nitro-*o*-xylene-5-sulphonyl chloride (SIMONSEN), T., 1146.

 C_9 Group.

- C_9H_{14} 1-Methyl-2-*isopropenyl*- Δ^1 -cyclopentene (HAWORTH), T., 1249; P., 193.

9 II

- C_9H_7N Quinoline, cupri-iodide of (DATTA), T., 432; P., 80.
- $C_9H_{11}N$ *N*-Methyldihydroisoindole (HOPE and LANKSHEAR), P., 224.

- $C_9H_{12}O_2$ 2:3-Dimethoxytoluene (CAIN and SIMONSEN), P., 380.
 $C_9H_{14}O_2$ 3-Ethoxy-1-methyl- Δ^3 -cyclohexen-5-one (GILLING), T., 2032.
 Acetyl derivative of 2:2:3:3-tetramethylbicyclo-[0,1,2]pentan-4-ol-5-one (FRANCIS and WILLSON), T., 2244.
 $C_9H_{14}O_3$ Acid, and its silver salt from oxidation of bornylene (HENDERSON and CAW), T., 1547; P., 246.
 $C_9H_{14}O_4$ α -Hydroxy- $\beta\gamma$ -tetramethylglutarolactone, and its silver salt (FRANCIS and WILLSON), T., 2243.
 $C_9H_{14}O_5$ α -Keto- $\beta\gamma$ -tetramethylglutaric acid, and its silver salt (FRANCIS and WILLSON), T., 2243.
 $C_9H_{16}O$ 1:1:2:2-Tetramethylcyclopentan-4-one (FRANCIS and WILLSON), T., 2245; P., 302.
 $C_9H_{16}O_4$ $\alpha\beta$ -Tetramethylglutaric acid (FRANCIS and WILLSON), T., 2245.
 $C_9H_{16}O_6$ $\gamma\epsilon\zeta$ -Trimethyl glucose (IRVINE and SCOTT), T., 574; P., 71.
 $\beta\gamma$ -Dimethyl methylglucoside (MACDONALD), T., 1903; P., 261.
 $\beta\gamma$ -Dimethyl- α -methylglucoside (IRVINE and SCOTT), T., 582; P., 71.
 $C_9H_{21}N$ Dimethyl-*n*- and *iso*-heptylamines, and their picrates (CLARKE), T., 1697.
 $C_9H_{22}N_2$ Tetramethylpentamethylenediamine, and its salts (CLARKE), T., 1701.

9 III

- $C_9H_6O_2Cl_4$ Acetyl derivative of 2:4:5:6-tetrachloro-*m*-cresol (CROWTHER and McCOMBIE), T., 547.
 $C_9H_7O_2Cl_3$ Acetyl derivative of 2:4:6-trichloro-*m*-cresol (CROWTHER and McCOMBIE), T., 546.
 $C_9H_7O_2I$ Iodocinnamic acids, investigation of (JAMES), T., 1368; P., 173.
 $C_9H_7O_2N$ 3- and 5-Nitro-4-methoxyphthalic acids (CAIN and SIMONSEN), P., 381.
 $C_9H_8O_4N_2$ Acetyl derivatives of *o*-, *m*-, and *p*-benzantialdioximes (BRADY and DUNN), T., 1624.
 $C_9H_9ON_3$ 3- and 4-Acetyl-3:4-tolylenediazoimides (MORGAN and MICKLETHWAIT), T., 1396; P., 232.
 $C_9H_9O_2N_3$ 3:5-Dicyano-2:6-diketo-4:4-dimethylpiperidine (THORPE and WOOD), T., 1592.
 $C_9H_9O_2Cl$ *p*-Methoxyphenylacetyl chloride (CAIN, SIMONSEN, and SMITH), T., 1036.
 $C_9H_9O_2I$ Methyl *o*-iodo-*p*-toluate (KENNER and WITHAM), T., 235.
 $C_9H_9O_3N$ *o*-Aldehydophenylglycine (GLUUD), T., 1251; P., 190.
 $C_9H_9O_3N_3$ 4-Acetoxybenzeneazoformamide (HEILBRON and HENDERSON), T., 1415.
 $C_9H_9O_4N$ *o*-Carbamylphenoxyacetic acid (MERRIMAN), T., 1844; P., 258.
 $C_9H_9O_5N$ 5- and 6-Nitro-2:3-dimethoxybenzoic acid (CAIN and SIMONSEN), P., 380.
 $C_9H_{10}O_3N_2$ Oxime of *o*-aldehydophenylglycine (GLUUD), T., 1253; P., 190.
 $C_9H_{11}ON$ *d*- and *l*-Hydroxyhydrindamines, hydrobromides of (POPE and READ), T., 447.
 $C_9H_{11}O_2N_3$ Oxime of *o*-aldehydophenylglycineamide (GLUUD), T., 1252; P., 190.
 $C_9H_{11}O_3N$ 5-Nitro-4-methoxy-*o*-xylene (CAIN and SIMONSEN), P., 381.
 $C_9H_{11}O_4N$ 5- and 6-Nitro-2:3-dimethoxytoluenes (CAIN and SIMONSEN), P., 380.
 $C_9H_{11}O_4N_3$ 4:6-Dinitro-3-methylamino-*o*-xylene (CROSSLEY and PRATT), T., 987.
 3:5-Dinitro-4-methylamino-*o*-xylene (CROSSLEY and PRATT), T., 985.

- $C_9H_{11}O_5N$ 2-Nitroveratryl alcohol (KAY and PICTET), T., 952.
- $C_9H_{12}ON_2$ 1-Hydroxy-2-hydrazinohydrindene, externally compensated, resolution of, and its salts (PEACOCK), T., 669; P., 109.
- $C_9H_{12}OBr_2$ Dibromophorone (FRANCIS and WILLSON), T., 2241.
- $C_9H_{12}O_2N_6$ Tolquinonedisemicarbazone (HEILBRON and HENDERSON), T., 1418.
- $C_9H_{12}O_4N_2$ 2-Nitro-5:6-dimethoxy-*m*-toluidine (CAIN and SIMONSEN), P., 380.
- $C_9H_{13}O_2Br$ 1-Bromo-2:2:3:3-tetramethylbicyclo[0,1,2]pentan-4-ol-5-one (FRANCIS and WILLSON), T., 2241; P., 302.
- $C_9H_{13}ON$ Ethyl ethoxyacetylcyanacetate, and its copper compound (WEIZMANN, STEPHEN, and AGASHE), T., 1856.
- $C_9H_{13}ON_3$ Semicarbazone of 2-acetyl-1-methyl- Δ^1 -cyclopentene (HAWORTH), T., 1249.
- $C_9H_{13}O_3N_3$ Nitrosodiallylaminopropionic acid (FRANKLAND and SMITH), T., 1002; P., 158.
- $C_9H_{16}ON_2$ Phenylmethylethylazonium hydroxide, and its salts, preparation of, and resolution of the iodide (SINGH), T., 604; P., 109.
- $C_9H_{16}O_2N_2$ Diallylaminopropionic acid, salts of (FRANKLAND and SMITH), T., 1002; P., 158.
- Nitrosotriacetaminine, catalytic decomposition of, by alkalis (FRANCIS and GEAKE), T., 1722; P., 249.
- $C_9H_{16}O_2N_6$ Disemicarbazones of 1- and 2-methyldihydroresorcin (GILLING), T., 2032.
- $C_9H_{19}O_2N$ Methyl 8-heptylcarbamate (PYMAN), T., 861.
- $C_9H_{19}O_3N_3$ Nitrosodipropylaminopropionic acid (FRANKLAND and SMITH), T., 1000; P., 158.
- $C_9H_{20}O_2N_2$ $\alpha\beta$ -Dipropylaminopropionic acid, salts of (FRANKLAND and SMITH), T., 998; P., 158.
- $C_9H_{21}ON$ Methyl ζ -dimethylaminohexyl ether, and its picrate (CLARKE), T., 1704.

9 IV

- $C_9H_{10}O_4NCl$ 2-Nitroveratryl chloride (KAY and PICTET), T., 953.
- $C_9H_{11}ONBr_2$ 2:6-Dibromo-4-trimethylammonium-1-benzoquinone (+ $3H_2O$), and its salts (MELDOLA and HOLLELY), T., 185.
- $C_9H_{11}ONI_2$ 2:6-Diiodo-4-trimethylammonium-1-benzoquinone (+ $3H_2O$), and its salts (MELDOLA and HOLLELY), T., 187.
- $C_9H_{11}O_3N_2Br$ 2-Bromo-6-nitro-4-trimethylammonium-1-benzoquinone (+ $2H_2O$) (MELDOLA and HOLLELY), T., 184.
- $C_9H_{11}O_3N_2I$ 2-Iodo-6-nitro-4-trimethylammonium-1-benzoquinone, and its chloride (MELDOLA and HOLLELY), T., 181.
- $C_9H_{16}O_2N_2Br_4$ Tetrabromodipropylaminopropionic acid (FRANKLAND and SMITH), T., 1003.

 C_{10} Group.

- $C_{10}H_{12}$ *iso*Butenylbenzene (THORPE and WOOD), T., 1578.
- $C_{10}H_{16}$ Bornylene, oxidation of, with hydrogen peroxide (HENDERSON and CAW), T., 1543; P., 246.
- Sylvestrene, constitution and derivatives of (HAWORTH, PERKIN, and WALLACH), T., 1228; P., 223.
- d*- and *l*-Sylvestrenes, synthesis of (HAWORTH and PERKIN), T., 2225; P., 356.
- Hydrocarbons, from geranyl chloride (FORSTER and CARDWELL), T., 1342, 1343; P., 244.

10 II

- $C_{10}H_8O$ β -Naphthol, constitution of (NOLAN and SMILES), P., 197.
- $C_{10}H_8N_2$ 2-Dipyridyl, absorption spectra of (PURVIS), T., 2283.
- $C_{10}H_{12}O_3$ Methyl *l*- α - and *dl*- β -hydroxy- β -phenylpropionates (McKENZIE and MARTIN), T., 114.
- $C_{10}H_{13}N$ *N*-Methyl-1:2:3:4-tetrahydroquinoline (*kairoline*), salts of (THORPE and WOOD), T., 1611.
- $C_{10}H_{14}O_2$ Camphorquinone, condensation of, with phenols (SEN-GUPTA and DEY), P., 155.
- $C_{10}H_{14}N_2$ Nicotine, absorption spectrum and constitution of (DOBBIE and FOX), T., 1193; P., 180.
- $C_{10}H_{16}O$ *l*-Epicamphor (BREDT and PERKIN), T., 2182; P., 356.
- $C_{10}H_{16}O_3$ Ethyl 2:6-dimethyl-2:3-dihydro-1:4-pyran-5-carboxylate (FARGHER and PERKIN), P., 72.
- Methyl ester of acid from oxidation of bornylene (HENDERSON and CAW), T., 1547; P., 246.
- $C_{10}H_{16}O_4$ Ethyl α - and β -methylglutaconates (THORPE and WOOD), T., 1582.
- $C_{10}H_{16}O_5$ Ethyl ethoxyacetylacetoacetate, and its copper compound (WEIZMANN, STEPHEN, and AGASHE), T., 1858.
- $C_{10}H_{16}N_2$ Substance, from β -aminocamphor and hydrazine (FORSTER and HOWARD), T., 67.
- $C_{10}H_{17}Cl$ Geranyl chloride (*o*-chloro- $\beta\zeta$ -dimethyl- $\Delta^{\beta\zeta}$ -octadiene) (FORSTER and CARDWELL), T., 1338; P., 244.
- $C_{10}H_{18}O$ *l*-Fenchyl alcohol, preparation of (PICKARD, LEWCOCK, and YATES), P., 127.
- Terpineol, isolation of, and its conversion into its acid esters (PICKARD, LEWCOCK, and YATES), P., 127.
- l*-Epiborneol (BREDT and PERKIN), T., 2222.
- l*- Δ^1 - and *d*- Δ^6 -*m*-Menthenol(8) (HAWORTH and PERKIN), T., 2233, 2237.
- $C_{10}H_{18}O_2$ Alcohols(2) from oxidation of bornylene (HENDERSON and CAW), T., 1549; P., 246.
- $C_{10}H_{18}O_6$ Methylglucoside- $\epsilon\zeta$ -monoacetone (MACDONALD), T., 1902; P., 261.
- $C_{10}H_{19}N$ *d*-*n*- and -*neo*Bornylamine, hydrobromides of (POPE and READ), T., 456.
- Geranylamine (*o*-amino- $\beta\zeta$ -dimethyl- $\Delta^{\beta\zeta}$ -octadiene) and its salts (FORSTER and CARDWELL), T., 1343; P., 244.
- $C_{10}H_{20}O$ Ethyl *n*-heptyl ketone (PICKARD and KENYON), T., 1945.
- $C_{10}H_{22}O$ Ethyl-*n*-heptylcarbinol, resolution of, and its salts (PICKARD and KENYON), T., 1945.
- $C_{10}H_{23}N$ Dimethyl-*n*- and -*iso*-octylamines, and their picrates (CLARKE), T., 1698.
- $C_{10}H_{24}N_2$ Tetramethylhexamethylenediamine, and its picrate (CLARKE), T., 1701.

10 III

- $C_{10}H_6O_3N_4$ 2:4:5-Trinitro- α -naphthylamine (RINDL), T., 1915; P., 264.
- $C_{10}H_9OCl_5$ 2:4:4:5-Tetrachloro-3-methyl-6- β -chloroisopropyl- $\Delta^{3:5}$ -cyclohexadienone (CROWTHER and MCCOMBIE), T., 544; P., 69.
- $C_{10}H_{10}O_2Br_2$ Acetyl derivative of 4:5-dibromo-3-*o*-xylenol (CROSSLEY and SMITH), T., 991; P., 170.
- $C_{10}H_{10}O_4N_2$ 2-Nitrohomoveratronitrile (KAY and PICTET), T., 954.
- $C_{10}H_{11}ON$ Styryl aminomethyl ketone, salts of (FOULDS and ROBINSON), T., 1768.

- $C_{10}H_{11}OCl_3$ 2:4:4-Trichloro-3-methyl-6-*iso*propyl- Δ^2 :5-*cyclohexadienone* (CROWTHER and MCCOMBIE), T., 543; P., 68.
- $C_{10}H_{11}O_2N$ 3-Amino-*p*-tolylacrylic acid (SALWAY), T., 1993; P., 287.
- $C_{10}H_{11}O_2N_3$ 3:5-Dicyano-2:6-diketo-4-methyl-4-ethylpiperidine (THORPE and WOOD), T., 1592.
- $C_{10}H_{11}O_2I$ Ethyl *o*-iodo-*p*-toluate (KENNER and WITHAM), T., 236.
- $C_{10}H_{11}O_4N_3$ Dinitro-*N*-methyl-1:2:3:4-tetrahydroquinoline (THORPE and WOOD), T., 1611.
- $C_{10}H_{11}O_6N$ 2-Nitrohomoveratric acid (KAY and PICTET), T., 955.
- $C_{10}H_{12}O_2Br_2$ Substance, from diazomethane and 5:5-dibromo-1:1:2:2-tetramethylcyclopentane-3:4-dione (FRANCIS and WILLSON), T., 2247.
- $C_{10}H_{12}N_6Fe$ α - and β -Tetramethylferrocyanides (HARTLEY), T., 1196; P., 188.
- $C_{10}H_{13}O_2N$ β -3-Amino-*p*-tolylpropionic acid (SALWAY), T., 1904; P., 287.
- $C_{10}H_{13}O_2N_3$ *dl*- and *l*-Hydroxy-2-semicarbazinohydrindene (PEACOCK), T., 673.
- $C_{10}H_{13}O_4N_3$ 4:6-Dinitro-3-dimethylamino-*o*-xylene (CROSSLEY and PRATT), T., 987.
- 3:5-Dinitro-4-dimethylamino-*o*-xylene (CROSSLEY and PRATT), T., 985.
- 4:6-Dinitro-3-ethylamino-*o*-xylene (CROSSLEY and PRATT), T., 987.
- 3:5-Dinitro-4-ethylamino-*o*-xylene (CROSSLEY and PRATT), T., 986.
- $C_{10}H_{14}O_5V$ Vanadium oxybisacetylacetonate (MORGAN and MOSS), T., 86.
- $C_{10}H_{15}OBr$ Bromo-*l*-epicamphor (BREDT and PERKIN), T., 2209.
- $C_{10}H_{15}O_2N$ α - and β -*iso*Nitroso-*l*-epicamphor (BREDT and PERKIN), T., 2211.
- Oximinio-derivatives of camphorquinone, configuration of (FORSTER), T., 662; P., 104.
- $C_{10}H_{15}O_2N_3$ γ -Allylaminoethyl- β -allylhydantoin, hydrochloride of (FRANKLAND and SMITH), T., 1003; P., 158.
- $C_{10}H_{16}O_4N_2$ Nitrosate of hydrocarbon, from geranyl chloride (FORSTER and CARDWELL), T., 1342; P., 244.
- $C_{10}H_{16}O_4Br_2$ Ethyl $\alpha\delta$ -dibromoadipate (STEPHEN and WEIZMANN), T., 271; P., 14.
- $C_{10}H_{17}ON$ Amino-*l*-epicamphor (BREDT and PERKIN), T., 2212.
- l*-Epicamphoroxime (BREDT and PERKIN), T., 2208.
- Substance, from heating β -aminocamphor (FORSTER and HOWARD), T., 68.
- $C_{10}H_{17}O_2N_3$ β -Allylamino- α -allylcarbamidopropionic acid (FRANKLAND and SMITH), T., 1003.
- $C_{10}H_{18}O_4N_2$ Nitrosate of hydrocarbon, from geranyl chloride (FORSTER and CARDWELL), T., 1343; P., 244.
- $C_{10}H_{18}O_4S_2$ Anhydride, from sulphur chloride and silver *isovalerate* (DENHAM and WOODHOUSE), T., 1866.
- $C_{10}H_{19}ON_3$ Semicarbazone of 1:1:2:2-tetramethylcyclopentan-4-one (FRANCIS and WILLSON), T., 2245.
- $C_{10}H_{19}O_2N_3$ γ -Propylaminomethyl- β -propylhydantoin, hydrochloride of (FRANKLAND and SMITH), T., 1001.
- $C_{10}H_{21}O_2N$ Ethyl δ -heptylcarbamate (PYMAN), T., 861.
- $C_{10}H_{21}O_3N_3$ β -Propylamino- α -propylcarbamidopropionic acid (FRANKLAND and SMITH), T., 1000.

10 IV

- $C_{10}H_4O_6N_3Cl$ 1-Chloro-2:4:5- and -2:4:8-trinitronaphthalenes (RINDL), T., 1912; P., 263.
- $C_{10}H_{12}ONBr$ Acetyl derivative of 6-bromo-*o*-4-xylylidine (CROSSLEY and BARTLETT), T., 1300.
- $C_{10}H_{17}O_4N_2Cl$ Nitrosate of geranyl chloride (FORSTER and CARDWELL), T., 1341; P., 244.

C₁₁ Group.

- C₁₁H₈O₆ Substance, from acetonedicarboxylic acid and pyrogallol (DEY), P., 154.
- C₁₁H₈N₂ Norisoharman, and its salts (PERKIN and ROBINSON), T., 1983.
- C₁₁H₉N 4-Phenylpyridine, absorption spectra of (PURVIS), T., 2284.
- C₁₁H₁₀N₂ Substance, from the oil of *Cydinus indicus* (WATSON), T., 550 ; P., 28.
- C₁₁H₁₀O₄ Ethyl coumaronecarboxylate, constitution of, and its ammonium salt (MERRIMAN), T., 1838 ; P., 257.
- C₁₁H₁₁N 4:7-Dimethylquinoline, and its picrate (EWINS and KING), T., 109.
4:8-Dimethylquinoline, and its salts (EWINS and KING), T., 107.
β-Cytisolidine (6:8-dimethylquinoline), synthesis of (EWINS), T., 102.
- C₁₁H₁₄O₃ Ethyl *p*-methoxyphenylacetate (CAIN, SIMONSEN, and SMITH), T., 1036.
Ethyl *o*-, *m*-, and *p*-tolylloxyacetates (HEWITT, JOHNSON, and POPE), T., 1629.
- C₁₁H₁₅N 4-Phenylpiperidine, absorption spectra of (PURVIS), T., 2285.
4:6- and 4:7-Dimethyl-1:2:3:4-tetrahydroquinolines, and their salts (EWINS and KING), T., 110.
4:8-Dimethyl-1:2:3:4-tetrahydroquinoline, and its picrate (EWINS and KING), T., 108.
N-Ethyl-1:2:3:4-tetrahydroquinoline, preparation of, and its salts (THORPE and WOOD), T., 1609.
α-Cytisolidine (6:8-dimethyl-1:2:3:4-tetrahydroquinoline), and its picrate (EWINS), T., 103.
- C₁₁H₁₆O₂ α- and β-Dihydroxy-α-phenylisopentanes, optically active (MCKENZIE and MARTIN), T., 114.
Oxymethylene-camphor, optically active and externally compensated forms of (POPE and READ), T., 445 ; P., 78.
d-Bornylene-3-carboxylic acid, preparation of, and its barium salt (BREDT and PERKIN), T., 2196.
l-Bornylene-2-carboxylic acid (BREDT and PERKIN), T., 2219.
- C₁₁H₁₆O₃ 3- and 4-Methylcyclohexane-1:1-diacetic anhydrides (THORPE and WOOD), T., 1595.
l-Epicamphorcarboxylic acid (BREDT and PERKIN), T., 2213.
- C₁₁H₁₆O₅ Ethyl phenoxyacetylacetate (WEIZMANN, STEPHEN, and AGASHE), T., 1859.
- C₁₁H₁₆O₇ Acetyl derivative from methylated cellulose (DENHAM and WOODHOUSE), T., 1741.
- C₁₁H₁₈O₂ *l*-Camphane-2-carboxylic acid (BREDT and PERKIN), T., 2219.
Camphane-3-carboxylic acid, preparation of (BREDT and PERKIN), T., 2198.
- C₁₁H₁₈O₃ *l*-Epiborneolcarboxylic acids (BREDT and PERKIN), T., 2216.
- C₁₁H₁₈O₄ Ethyl α-dimethylglutaconate (THORPE and WOOD), T., 1757.
Ethyl α-ethylglutaconate (THORPE and WOOD), T., 1582.
Ethyl 1-methylcyclobutane-2:2-dicarboxylate (BLACKSTOCK and PERKIN), P., 74.
3- and 4-Methylcyclohexane-1:1-diacetic acids, and their salts (THORPE and WOOD), T., 1595 ; P., 256.
- C₁₁H₁₈O₆ Ethyl ethoxyacetylmalonate, and its copper compound (WEIZMANN, STEPHEN, and AGASHE), T., 1858.
- C₁₁H₂₂O Ethyl *n*-octyl ketone (PICKARD and KENYON), T., 1946.
- C₁₁H₂₂O₃ α-Hydroxy-*n*-undecolic acid (PICKARD and KENYON), T., 1947.
- C₁₁H₂₄O Ethyl-*n*-octylcarbinol, resolution of (PICKARD and KENYON), T., 1946.
- C₁₁H₂₆N₂ Tetramethylheptamethylenediamine, and its picrate (CLARKE), T., 1701.

11 III

- $C_{11}H_7O_3N_3$ 2:4:5-Trinitro- α -naphthyl methyl ether (RINDL), T., 1916; P., 264.
- $C_{11}H_7N_2Cl$ Chloronor α isoharman (PERKIN and ROBINSON), T., 1981.
- $C_{11}H_9ON_2$ Lactam of 2-aminoquinoline-3-acetic acid (PERKIN and ROBINSON), T., 1982.
- $C_{11}H_9O_3N$ Carbostyryl-3-acetic acid (PERKIN and ROBINSON), T., 1980.
- $C_{11}H_9O_4N$ α -Cyanomeconine (G. M. and R. ROBINSON), P., 267.
- $C_{11}H_{10}O_2N_2$ Carbostyryl-3-acetamide (PERKIN and ROBINSON), T., 1981.
- $C_{11}H_{11}ON$ 2-Hydroxy-4:8-dimethylquinoline (EWINS and KING), T., 107.
- 3-Acetyl-2-methylindole (SALWAY), T., 354.
- $C_{11}H_{11}O_3Na$ Ethyl sodiobenzoylacetate, action on α -dibromobutane on (FARGHER and PERKIN), P., 72.
- $C_{11}H_{11}O_4N$ α -Aldehydosuccinanic acid (PERKIN and ROBINSON), T., 1979.
- $C_{11}H_{11}O_6N_3$ Diacetyl derivative of 4:6-dinitroguaiacol (MELDOLA and REVERDIN), T., 1489.
- $C_{11}H_{12}ON_2$ Oxime of 3-acetyl-2-methylindole (SALWAY), T., 355.
- $C_{11}H_{12}O_7N_4$ Diacetyl derivative of 3:5-dinitro-2:4-diaminoanisole (MELDOLA and REVERDIN), T., 1490.
- $C_{11}H_{13}O_2N$ Acetoaceto-*o*-, *m*-, and *p*-toluidides (EWINS and KING), T., 106.
- $C_{11}H_{14}ON_2$ α -Benzoylamino- γ -methyleneaminopropane (TITHERLEY and BRANCH), T., 338; P., 29.
- Benzoylhexahydropyrimidine, salts of (TITHERLEY and BRANCH), T., 338.
- Cytisine, constitution of (EWINS), T., 97.
- $C_{11}H_{14}OCl_2$ 2:6-Dichlorothymol methyl ether (CROWTHER and McCOMBIE), T., 544; P., 68.
- $C_{11}H_{14}O_4N_3$ Dinitro-*N*-ethyl-1:2:3:4-tetrahydroquinoline (THORPE and WOOD), T., 1610.
- $C_{11}H_{15}OCl$ Bornylene-3-carboxyl chloride (BREDT and PERKIN), T., 2197.
- $C_{11}H_{16}O_2N_3$ 4-Hydroxy-2-methyl-5-*iso*propylbenzeneazoformamide, and its sodium salt (HEILBRON and HENDERSON), T., 1419.
- $C_{11}H_{16}O_3Br$ Acetyl derivative of 1-bromo-2:2:3:3-tetramethylbicyclo[0,1,2,]pentan-4-ol-5-one (FRANCIS and WILLSON), T., 2242.
- α -Bromo-*l*-epicamphorcarboxylic acid (BREDT and PERKIN), T., 2215.
- $C_{11}H_{16}O_4Br$ Carbomethoxy-derivative of 1-bromo-2:2:3:3-tetramethylbicyclo[0,1,2,]pentan-4-ol-5-one (FRANCIS and WILLSON), T., 2242.
- $C_{11}H_{17}ON$ Bornylene-3-carboxylamide (BREDT and PERKIN), T., 2197.
- $C_{11}H_{17}ON_2$ *l*-Bornylene-2-hydroxamic acid (BREDT and PERKIN), T., 2221.
- $C_{11}H_{17}O_2N$ Imides of 3- and 4-methylcyclohexane-1:1-diacetic acids (THORPE and WOOD), T., 1595.
- Camphorcarboxylamide, isomeric changes in (LOWRY and GIBSON), T., 913.
- α -Bornylene-3-hydroxamic acid (BREDT and PERKIN), T., 2203.
- $C_{11}H_{18}ON_2$ α -Bornylene-3-carboxylic hydrazide, and its hydrochloride (BREDT and PERKIN), T., 2202.
- Camphorquinone α - and β -methylhydrazones (FORSTER and CARDWELL), T., 867; P., 150.
- $C_{11}H_{18}ON_3$ *l*-Epicamphorsemicarbazone (BREDT and PERKIN), T., 2209.
- $C_{11}H_{19}O_2N$ Substance ($+ \frac{1}{2} H_2O$), from *isonitrosoepicamphor* and magnesium methyl iodide (FORSTER), T., 669.
- $C_{11}H_{19}O_2N_3$ α - and β -Semicarbazones of β -hydroxycamphor (FORSTER and HOWARD), T., 69.
- $C_{11}H_{20}ON_2$ Carbamide from geranylamine (FORSTER and CARDWELL), T., 1344.
- $C_{11}H_{20}O_3N_4$ 1:7-Dipropyltetrahydrouric acid (FRANKLAND and SMITH), T., 1001; P., 158.

$C_{11}H_{21}O_2Br$ α -Bromo-*n*-undecic acid (PICKARD and KENYON), T., 1947.

$C_{11}H_{24}ON_2$ *s*-Di- γ -amylcarbamide (PYMAN), T., 857.

11 IV

$C_{11}H_{10}ONCl$ 3-Chloroacetyl-2-methylindole (SALWAY), T., 354.

$C_{11}H_{11}ON_4Cl$ 1-Phenyl-2:3-dimethylpyrazolone-4-diazonium chloride, aurichloride (MORGAN and REILLY), T., 814

$C_{11}H_{13}O_2N_3Br_2$ Dibromo-4-hydroxy-2-methyl-5-*isopropyl*benzeneazoformamide (HEILBRON and HENDERSON), T., 1420.

$C_{11}H_{14}O_2N_3Br$ 3-Bromo-4-hydroxy-2-methyl-5-*isopropyl*benzeneazoformamide (HEILBRON and HENDERSON), T., 1419.

C_{12} Group.

$C_{12}H_{10}$ Acenaphthene, refractivity of (CROMPTON and SMYTH), T., 1302; P., 224.

$C_{12}O_9$ Mellitic anhydride (JARRARD), P., 106.

12 II

$C_{12}H_6O_{12}$ Mellitic acid, and its salts (JARRARD), P., 106.

$C_{12}H_6Br_2$ Dibromodiphenylene (DOBBIE, FOX, and GAUGE), T., 39.

$C_{12}H_9Cl$ 3-Chloroacenaphthene, refractivity of (CROMPTON and SMYTH), T., 1303; P., 224.

$C_{12}H_9Br$ 3-Bromoacenaphthene, refractivity of (CROMPTON and SMYTH), T., 1303; P., 224.

$C_{12}H_9I$ 3-Iodoacenaphthene, refractivity of (CROMPTON and SMYTH), T., 1304; P., 224.

$C_{12}H_{10}O_2$ 2-Phenyl-6-methyl-4-pyrone, attempted resolution of the salts of (LEVY, HOLMYARD, and RUHEMANN), P., 159.

$C_{12}H_{10}O_3$ 6-Hydroxy-4-phenyl-3-methyl-2-pyrone (THORPE and WOOD), T., 1576.

$C_{12}H_{10}O_4$ Substance, from acetonedicarboxylic acid and *p*-cresol (DEY), P., 154.

$C_{12}H_{10}O_5$ Substance, from orcinol and acetonedicarboxylic acid (DEY), P., 154.

$C_{12}H_{10}N_2$ *iso*Harman, synthesis of, and its salts (PERKIN and ROBINSON), T., 1973; P., 290.

$C_{12}H_{12}O_4$ β -Phenyl- α -methylglutaconic acids, and their salts (THORPE and WOOD), T., 1575; P., 253.

$C_{12}H_{13}N_3$ Acetone-2-quinolylhydrazine (PERKIN and ROBINSON), T., 1978.

$C_{12}H_{14}O_2$ α -Phenylhexane- α -dione (FARGHER and PERKIN), P., 73.

$C_{12}H_{14}O_4$ Ethyl *p*-methoxyphenylpyruvate (CAIN, SIMONSEN, and SMITH), T., 1036.

$C_{12}H_{16}O_2$ α -Phenylhexane- ϵ -ol- α -one (FARGHER and PERKIN), P., 73.

$C_{12}H_{16}O_3$ Ethyl 3:4-dimethoxyphenylacetate (CAIN, SIMONSEN, and SMITH), T., 1038.

$C_{12}H_{16}O_5$ Methoxymethylfisetol dimethyl ether (PERKIN), T., 1636; P., 253.

$C_{12}H_{16}O_6$ Gossypitol tetramethylether (PERKIN), T., 658; P., 110.

$C_{12}H_{17}N$ 1:6:8-Trimethyl-1:2:3:4-tetrahydroquinoline, hydriodide of (EWINS), T., 104.

$C_{12}H_{18}O_2$ Methyl bornylene-2- and -3-carboxylates (BREDT and PERKIN), T., 2198, 2218.

$C_{12}H_{20}O_2$ Geranylacetic acid (FORSTER and CARDWELL), T., 1346.

$C_{12}H_{20}O_4$ *cis*-Ethyl $\alpha\alpha\beta$ -trimethylglutaconate (THORPE and WOOD), T., 1759.

$C_{12}H_{22}O$ Geranylethyl ether (FORSTER and CARDWELL), T., 1342.

$C_{12}H_{22}O_6$ γ - ϵ -Trimethyl glucosemonacetone (IRVINE and SCOTT), T., 574; P., 71.

β - γ -Dimethyl methylglucoside- ϵ -monoacetone (MACDONALD), T., 1903; P., 261.

$C_{12}H_{26}O$ Ethyl-*m*-nonylcarbinol, resolution of, and its salts (PICKARD and KENYON), T., 1947.

12 III

$C_{12}H_4O_8N_4$ Tetranitrodiphenylene (DOBBIE, FOX, and GAUGE), T., 39.

$C_{12}H_6O_2N_4$ Bisbenz \textit{isoox} adiazole (GREEN and ROWE), T., 2028; P., 276.

$C_{12}H_6O_4N_2$ Dinitrodiphenylene (DOBBIE, FOX, and GAUGE), T., 40.

$C_{12}H_6O_4N_4$ Bisbenz \textit{isoox} adiazole oxide (GREEN and ROWE), T., 2026; P., 276.

Substance, from oxidation of dinitrobenzidine (m.p. 233°) (GREEN and ROWE), T., 2028; P., 276.

$C_{12}H_6O_{10}N_6$ Tetranitro-*p*-azophenol (ROBERTSON), T., 1476.

$C_{12}H_8O_6N_2$ 3:3'- and 3:5'-Dinitro-4:4'-diphenols (CAIN, COULTHARD, and MICKLETHWAIT), T., 2083.

$C_{12}H_8O_6N_4$ Dinitro-*p*-azophenol (ROBERTSON), T., 1476.

$C_{12}H_9NSe$ Selenodiphenylamine (WEIZMANN and STEPHEN), P., 196.

$C_{12}H_{10}O_2N_2$ *p*-Azophenol, isomerism of (ROBERTSON), T., 1472; P., 221.

$C_{12}H_{10}O_4N_4$ *o*-Dinitrobenzidines, absorption spectra and constitution of the (CAIN, MACBETH, and STEWART), T., 586; P., 77; derivatives of (CAIN, COULTHARD, and MICKLETHWAIT), T., 2074; P., 289.

Diphenoquinonetetraoxime (GREEN and ROWE), T., 2027; P., 276.

$C_{12}H_{10}O_6N_4$ 2:4:5-Trinitro-*a*-naphthyldimethylamine (RINDL), T., 1916.

2:4:5-Trinitro-*a*-naphthylethylamine (RINDL), T., 1916.

$C_{12}H_{11}O_3N$ Methyl carbostyryl-3-acetate (PERKIN and ROBINSON), T., 1981.

$C_{12}H_{12}O_2Si$ Diphenylsilicanediol, condensation products of (KIPPING and ROBISON), P., 374.

$C_{12}H_{13}O_3N_3$ ω -Imide of $\alpha\alpha'$ -dicyanocyclohexane-1:1-diacetic acid (THORPE and WOOD), T., 1592.

$C_{12}H_{15}ON$ Benzoylpiperidine, absorption spectra of (PURVIS), T., 2285.

$C_{12}H_{15}OBr$ ϵ -Bromo-*a*-phenylhexan- α -one (FARGHER and PERKIN), P., 73.

$C_{12}H_{15}O_3N$ Monoacetyl derivative of β -3-amino-*p*-tolylpropionic acid (SALWAY), T., 1904.

2:4-Xylylsuccinamic acid (SALWAY), T., 1991; P., 287.

$C_{12}H_{16}ON_2$ Methyleytosine, and its picrate (POWER and SALWAY), T., 191; P., 2.

$C_{12}H_{16}O_2N_2$ 2:4-Xylylsuccinamide (SALWAY), T., 1992.

$C_{12}H_{17}O_2N$ Ethyl β -3-amino-*p*-tolylpropionate, and its hydrochloride (SALWAY), T., 1904.

Ethyl phenylethylaminooacetate, and its platinichloride (THORPE and WOOD), T., 1607.

$C_{12}H_{17}O_3N$ α -Dimethylamino- γ -phenoxybutyric acid, and its salts (SALWAY), T., 357.

$C_{12}H_{18}O_3V$ Vanadium oxybisacetylmethylacetate (MORGAN and MOSS), T., 88.

$C_{12}H_{19}O_4N$ Ethyl α -cyano- $\beta\beta$ -dimethylpropanedicarboxylate (THORPE and WOOD), T., 1583.

$C_{12}H_{19}O_6N$ Ethyl glycerylmethylenemalonate (LEVY), P., 353.

$C_{12}H_{21}ON$ Acetyl derivative of geranylamine (FORSTER and CARDWELL), T., 1344.

$C_{12}H_{26}ON$ Tetrapropylammonium hydroxide, cupri-iodide of (DATTA), T., 432; P., 80.

12 IV

- $C_{12}H_6O_2N_2Br_4$ α - and β -Tetrabromo-*p*-azophenols (ROBERTSON), T., 1477.
 $C_{12}H_6O_2N_2Cl_2$ 4:4'-Dichloro-3:3'-dinitrodiphenyl (CAIN, COULTHARD, and MICKLETHWAIT), T., 2080.
 $C_{12}H_6O_4N_2Br_2$ 4:4'-Dibromo-3:3'- and -3:5'-dinitrodiphenyl (CAIN, COULTHARD, and MICKLETHWAIT), T., 2081.
 $C_{12}H_6O_4N_2I_2$ 4:4'-Di-iodo-3:3'- and -3:5'-dinitrodiphenyl (CAIN, COULTHARD, and MICKLETHWAIT), T., 2082.
 $C_{12}H_6O_6N_4Br_2$ Dibromodinitro-*p*-azophenol (ROBERTSON), T., 1477.
 $C_{12}H_7O_2Cl_2I_3$ 2:4:6-Tri-iodophenylbenzoate dichloride (KING and MCCOMBIE), T., 227.
 $C_{12}H_{10}O_2N_2Br_2$ *p*-Azophenol perbromide (ROBERTSON), T., 1477.
 $C_{12}H_{14}O_2NBr$ Diacetyl derivative of 6-bromo-*o*-4-xylydine (CROSSLEY and BARTLETT), T., 1301.

C_{13} Group.

- $C_{13}H_{12}O_5$ Ethyl acetocoumaranonecarboxylate (MERRIMAN), T., 1843.
 $C_{13}H_{13}O_8$ 3:4:5:7-Tetrahydroxy-2-*m*-*p*-dihydroxyphenyl-1:4-benzopyran (WATSON and SEN), P., 349.
 $C_{13}H_{14}O_3$ 6-Phenyl-2-methyl-2:3-dihydro-1:4-pyran-5-carboxylic acid (FARGHER and PERKIN), P., 73.
 Xanthohumol (POWER, TUTIN, and ROGERSON), T., 1288; P., 181.
 $C_{13}H_{18}O_6$ Diacetyl derivative of 5:5-dibromo-1:1:2:2-tetramethylcyclopentane-3:4-dione (FRANCIS and WILLSON), T., 2246.
 $C_{13}H_{20}O_2$ α - β -Dihydroxy- α -phenyl- γ -ethyl-*n*-pentane (MCKENZIE and MARTIN), T., 118.
 Ethyl bornylene-3-carboxylate (BREDT and PERKIN), T., 2198.
 $C_{13}H_{23}O_2$ Methyl geranylacetate (FORSTER and CARDWELL), T., 1346.
 $C_{13}H_{25}O_5$ Ethyl amyloxyacetylacetoacetate (WEIZMANN, STEPHEN, and AGASHE), T., 1859.
 $C_{13}H_{26}O_6$ Monomethyl glucosediacetone (IRVINE and SCOTT), T., 570; P., 70.
 $C_{13}H_{22}O_{10}$ Substance, from methylation of cellulose (DENHAM and WOODHOUSE), T., 1738; P., 251.
 $C_{13}H_{26}O$ Ethyl *n*-decyl ketone (PICKARD and KENYON), T., 1948.
 $C_{13}H_{28}O$ Ethyl-*n*-decylcarbinol, and its resolution and salts (PICKARD and KENYON), T., 1948.

13 III

- $C_{13}H_{11}O_6N_3$ 3:5-Dinitro-2-phenoxy-*p*-anisidine (MELDOLA and REVERDIN), T., 1491.
 $C_{13}H_{12}ON_2$ Harmine, constitution of (PERKIN and ROBINSON), T., 1973; P., 290.
 $C_{13}H_{13}ON$ Ethyl phenoxyacetylcyanoacetate, and its copper compound (WEIZMANN, STEPHEN, and AGASHE), T., 1856.
 $C_{13}H_{14}ON_2$ Harmaline, constitution of (PERKIN and ROBINSON), T., 1973; P., 290.
 $C_{13}H_{15}ON$ 2-Methyldihydroresorcinanilide (GILLING), T., 2034.
 $C_{13}H_{15}O_2N_3$ ω -Imides of $\alpha\alpha'$ -dicyano-3- and 4-methylcyclohexane-1:1-diacetic acids (THORPE and WOOD), T., 1593, 1597.
 $C_{13}H_{16}ON_2$ 3-Dimethylaminoacetyl-2-methylindole, and its hydrochloride (SALWAY), T., 355; P., 59.
 $C_{13}H_{16}O_4N_2$ Diimides of 3- and 4-methylcyclohexane-1:1-dimalonic acids (THORPE and WOOD), T., 1594.

- $C_{13}H_{17}O_3N$ Methyl 2:4-xylylsuccinamate (SALWAY), T., 1991; P., 287.
- $C_{13}H_{17}O_3N_3$ ω -Imide of α -cyano- α' -carbamyl-4-methylcyclohexane-1:1-diacetic acid (THORPE and WOOD), T., 1593.
- $C_{13}H_{17}O_4N_3$ 4:6-Dinitro-3-piperidino-*o*-xylene (CROSSLEY and PRATT), T., 988.
3:5-Dinitro-4-piperidino-*o*-xylene (CROSSLEY and PRATT), T., 986.
Semicarbazone of ethyl-*p*-methoxyphenylpyruvate (CAIN, SIMONSEN, and SMITH), T., 1036.
- $C_{13}H_{17}O_6N$ α -Aminohelicin, hydrochloride of (IRVINE and HYND), T., 54.
- $C_{13}H_{18}ON_2$ 2- α -Dimethylamino- γ -hydroxypropylindole, and its salts (SALWAY), T., 360; P., 59.
- $C_{13}H_{18}O_2N_4$ ω -Imino-imide of α -cyano- α' -carbamyl-4-methylcyclohexane-1:1-diacetic acid and its platinichloride (THORPE and WOOD), T., 1592.
Di-imino-di-imides of 3- and 4-methylcyclohexane-1:1-dimalonic acids and their platinichlorides (THORPE and WOOD), T., 1594.
- $C_{13}H_{19}O_3N$ Methyl α -dimethylamino- γ -phenoxybutyrate, hydrochloride of (SALWAY), T., 358.
Acetylbornylene-3-hydroxamic acid (BREDT and PERKIN), T., 2205.
- $C_{13}H_{19}O_5N$ α -Aminobenzylglucoside, hydrochloride of (IRVINE and HYND), T., 53.
- $C_{13}H_{19}O_6N$ α -Aminosalicin, hydrochloride of (IRVINE and HYND), T., 54.
- $C_{13}H_{22}O_4Br_2$ Ethyl $\alpha\gamma$ -dibromoazelaate (LE SUEUR), T., 1124.
- $C_{13}H_{28}ON_2$ *s*-Di- γ -hexylcarbamide (PYMAN), T., 857.

13 IV

- $C_{13}H_5O_2Cl_4Br$ Benzoyl derivative of 2:3:4:6-tetrachloro-5-bromophenol (McCOMBIE and WARD), T., 2005.
- $C_{13}H_5O_2Cl_4I$ Benzoyl derivative of 2:3:4:6-tetrachloro-5-iodophenol (McCOMBIE and WARD), T., 2004.
- $C_{13}H_6O_2Cl_3Br$ Benzoyl derivative of 2:4:6-trichloro-3-bromophenol (McCOMBIE and WARD), T., 2005.
- $C_{13}H_6O_2Cl_3I$ Benzoyl derivative of 2:4:6-trichloro-3-iodophenol (McCOMBIE and WARD), T., 2003.
- $C_{13}H_7O_2Cl_2I_2$ 6-Chloro-2:4-di-iodophenyl benzoate dichloride (KING and McCOMBIE), T., 231.
- $C_{13}H_7O_2Br_2I$ 2:6-Dibromo-4-iodophenyl benzoate (KING and McCOMBIE), T., 228.
- $C_{13}H_8O_2Cl_2I_2$ 2:4-Di-iodophenyl benzoate dichloride (KING and McCOMBIE), T., 229.
- $C_{13}H_9O_4N_2Br$ Benzoyl derivative of bromonitro-*p*-aminophenol (MELDOLA and HOLLELY), T., 183.
- $C_{13}H_{10}ONI$ Benzoyl-*m*-iodoaniline (McCOMBIE and WARD), T., 2000.
- $C_{13}H_{10}O_2NBr$ Benzoyl derivative of 2-bromo-4-aminophenol (MELDOLA and HOLLELY), T., 182.
- $C_{13}H_{11}O_2N_2S$ 3- and 4-Benzenesulphonyl-3:4-tolylenediazoimides (MORGAN and SCHARFF), P., 374.
- $C_{13}H_{13}O_2N_2S$ 3- and 4-Benzenesulphonyl-3:4-tolylenediamines (MORGAN and SCHARFF), P., 374.

13 V

- $C_{13}H_7ONCl_3I$ Benzoyl-2:4:6-trichloro-3-iodoaniline (McCOMBIE and WARD), T., 2001.
- $C_{13}H_7O_2Cl_2Br_2I$ 2:6-Dibromo-4-iodophenyl benzoate dichloride (KING and McCOMBIE), T., 228.
- $C_{13}H_8ONCl_2I$ Benzoyl-2:4-dichloro-5-iodoaniline (McCOMBIE and WARD), T., 2000; P., 283.

$C_{13}H_{11}O_4N_4SNa$ Substance, from sodium methylaniline- ω -sulphonate and diazotised *p*-nitroaniline (POPE and WILLET), T., 1261.

C_{14} Group.

$C_{14}H_{14}$ 2:2'-Dimethyldiphenyl (*ditolyl*), formation of cyclic compounds from derivatives of (KENNER), T., 613; P., 105.

14 II

$C_{14}H_8O_5$ 2:7:7-Trihydroxyphenanthraquinone (MUKERJEE and WATSON), P., 269.

$C_{14}H_{10}O_3$ Benzoic anhydride, rate of hydration of (WILSDON and SIDGWICK), T., 1959; P., 265.

$C_{14}H_{12}O$ Deoxybenzoin, synthesis of unsymmetrical derivatives of (CAIN, SIMONSEN, and SMITH), T., 1035; P., 172.

$C_{14}H_{16}N_2$ $\omega\omega'$ -Diamino-2:2'-dimethyldiphenyl, dihydrochlorides of (KENNER), T., 627.

$C_{14}H_{18}O_6$ $\epsilon\delta$ - and δ -Benzylidene α -methylglucosides (IRVINE and SCOTT), T., 580; P., 71.

Hydroxytriethoxybenzeneglyoxylic acid (*gossypetonic acid*) (PERKIN), T., 656; P., 110.

$C_{14}H_{22}O_8$ Ethyl $\alpha\delta$ -diacetoxyadipate (STEPHEN and WEIZMANN), T., 272.

$C_{14}H_{24}O_5$ Ethyl β -amyloxypropionylacetoacetate (WEIZMANN, STEPHEN, and AGASHE), T., 1860.

$C_{14}H_{28}O$ Ethyl *n*-undecyl ketone (PICKARD and KENYON), T., 1950.

$C_{14}H_{30}O$ Ethyl-*n*-undecylcarbinol, and its resolution and salts (PICKARD and KENYON), T., 1951.

14 III

$C_{14}H_6O_4N_4$ 3:3-Dinitro-4:4'-dicyanodiphenyl (CAIN, COULTHARD, and MICKLETHWAIT), T., 2082.

$C_{14}H_7ON$ Nitro-2:7-dihydroxyphenanthraquinone (MUKERJEE and WATSON), P., 268.

$C_{14}H_8O_2Cl_4$ Benzoyl derivative of 2:4:5:6-tetrachloro-*m*-cresol (CROWTHER and McCOMBIE), T., 547.

$C_{14}H_8O_3Br_2$ *o*-Bromobenzoic anhydride, preparation of (DENHAM and WOODHOUSE), T., 1868.

$C_{14}H_8O_7N_2$ *m*-Nitrobenzoic anhydride, preparation of (DENHAM and WOODHOUSE), T., 1868.

$C_{14}H_9O_4N$ Amino-2:7-dihydroxyphenanthraquinone (MUKERJEE and WATSON), P., 268.

$C_{14}H_{10}O_6N_4$ 3:3'- and 3:5'-Dinitrodiformylbenzidines (CAIN, COULTHARD, and MICKLETHWAIT), T., 2077.

$C_{14}H_{11}ON_3$ 3- and 4-Benzoyl-3:4-tolylenediazoimides (MORGAN and MICKLETHWAIT), T., 1402; P., 232.

$C_{14}H_{12}O_2N_2$ Benzildioximes, nickel compounds of (ATAK), T., 1317; P., 195.

$C_{14}H_{13}ON$ α -Keto- β -anilino- α -phenylethane, condensation of, and its homologues, with carbonyl chloride, phenylcarbimide, and phenylthiocarbimide (McCOMBIE and SCARBOROUGH), T., 56.

Desylamine, derivatives of (McKENZIE and BARROW), T., 1331; P., 228.

$C_{14}H_{13}O_4N_3$ 3:5-Dinitro-4-anilino-*o*-xylene (CROSSLEY and PRATT), T., 986.

4:6-Dinitro-3-anilino-*o*-xylene (CROSSLEY and PRATT), T., 987.

$C_{14}H_{13}O_5N$ Ethyl phthaliminoacetoacetate, isomeric forms of (WEIZMANN, STEPHEN, and AGASHE), T., 1860.

- $C_{14}H_{13}NS$ *N*- and *S*-Methylthiobenzanilides, T., 2274; P., 360.
 $C_{14}H_{14}ON_2$ 3-Benzoyl-3:4-tolylenediamine (MORGAN and MICKLETHWAIT), T., 1403; P., 232.
 $C_{14}H_{14}OSn$ Di-*p*-tolylstannic oxide (SMITH and KIPPING), T., 2050.
 Dibenzylstannic oxide (SMITH and KIPPING), T., 2045.
 $C_{14}H_{14}Cl_2Sn$ Dichlorodi-*p*-tolylstannane (SMITH and KIPPING), T., 2049.
 $C_{14}H_{17}O_4N$ Diacetyl derivative of β -3-amino-*p*-tolylpropionic acid (SALWAY), T., 1904.
 $C_{14}H_{19}O_4N$ Ethyl anilinodiacetate (THORPE and WOOD), T., 1607.
 $C_{14}H_{21}O_6N$ Ethyl α -cyanoisobutane- $\alpha\gamma\gamma$ -tricarboxylate (THORPE and WOOD), T., 1581.
 $C_{14}H_{22}O_5N_2$ $\beta\gamma$ -Dimethyl glucosephenylhydrazone (IRVINE and SCOTT), T., 585.
 $C_{14}H_{23}O_8N$ Triacetyl- α -aminoethylglucoside, hydrobromide of (IRVINE and HYND), T., 49.

14 IV

- $C_{14}H_8O_4N_4S_2$ 3:3'-Dinitro-4:4'-dithiocyanodiphenyl (CAIN, COULTHARD, and MICKLETHWAIT), T., 2083.
 $C_{14}H_8O_4Br_2S_2$ Anhydrides, from sulphur chloride and silver bromobenzoates (DENHAM and WOODHOUSE), T., 1867.
 $C_{14}H_8O_8N_2S_2$ Anhydrides, from sulphur chloride and silver nitrobenzoates (DENHAM and WOODHOUSE), T., 1867.
 $C_{14}H_{10}O_2N_2Ni$ Nickel compound of γ -benzildioxime (ATACK), T., 1321; P., 195.

 C_{15} Group.

- $C_{15}H_{12}$ 3:5-Dibenzo- $\Delta^{1:3:5}$ -cycloheptatriene, and its picrate (KENNER), T., 625; P., 106.

15 II

- $C_{15}H_8O_8$ Gossypitone (PERKIN), T., 657; P., 110.
 $C_{15}H_{10}O_4$ Methyl- α - and - β -naphthacoumarincarboxylic acids (DEY), P., 154.
 $C_{15}H_{10}O_7$ Quercetin, methylation of (PERKIN), T., 1632; P., 253; colouring matters from (WATSON and SEN), P., 349.
 $C_{15}H_{10}O_8$ Gossypetin (PERKIN), T., 650; P., 110.
 Quercetagetin (+ $2H_2O$), and its sulphate (PERKIN), T., 209; P., 9.
 $C_{15}H_{14}O_5$ 2:2'-Dihydroxy-3:4-dimethoxybenzophenone (SEN-GUPTA and WATSON), P., 270.
 Acid, from hydrolysis of humulol (POWER, TUTIN, and ROGERSON), T., 1288.
 $C_{15}H_{14}N_5$ 3:5-Dimethylpyrazole-4-azo- β -naphthylamine (MORGAN and REILLY), P. 379.
 $C_{15}H_{15}N$ 1-Amino-3:5-dibenzo- $\Delta^{3:5}$ -cycloheptadiene and its salts (KENNER), T., 623; P., 105.
 $C_{15}H_{16}O_4$ Substance, from hydroxyperezone (REMFY), T., 1085.
 $C_{15}H_{20}O_3$ Perezone (REMFY), T., 1076; P., 72.
 Pipitzol (REMFY), T., 1079.
 $C_{15}H_{22}O_5$ Ethyl dicarboxylglutaconate, action of amino-acid esters on (LEVY), P., 353.
 $C_{15}H_{24}O_3$ Tetrahydropipitzol (REMFY), T., 1083.
 $C_{15}H_{24}O_8$ Ethyl $\alpha\delta$ -diacetoxy- β -methyladipate (STEPHEN and WEIZMANN), T., 273.
 $C_{15}H_{26}O_8$ Ethyl β -amyloxypropionylmalonate (WEIZMANN, STEPHEN, and AGASHE), T., 1860.

- $C_{15}H_{30}O$ Ethyl-*n*-dodecyl ketone (PICKARD and KENYON), T., 1952.
 $C_{15}H_{32}O$ Ethyl-*n*-dodecylcarbinol, and its resolution and salts (PICKARD and KENYON), T., 1951.

15 III

- $C_{15}H_{11}O_2N$ 3:5-Diphenyl-2:3-dihydro-2-oxazolone (McCOMBIE and SCARBOROUGH), T., 58.
 $C_{15}H_{11}O_7N$ 6'-Aminoquercetin (WATSON), P., 280.
 $C_{15}H_{12}O_2Br_2$ Benzoyl derivative of 4:5-dibromo-3-*o*-xylenol (CROSSLEY and SMITH), T., 991; P., 170.
 $C_{15}H_{12}O_3N_2$ Benzenehydrazocarbonylcoumaranone (MERRIMAN), T., 1851; P., 258.
 $C_{15}H_{13}ON_4$ 3:5-Dimethylpyrazole-4-azo- β -naphthol (MORGAN and REILLY), P., 379.
 $C_{15}H_{13}O_2Br$ Benzoyl derivative of 5-bromo-*o*-3-xylenol (CROSSLEY), T., 2182; P., 352.
 Benzoyl derivatives of 5- and 6-bromo-*o*-4-xylenols (CROSSLEY and BARTLETT), T., 1299; P., 217.
 $C_{15}H_{13}ON_2$ Benzilmethylhydrazone (FORSTER and CARDWELL), T., 868; P., 150.
 $C_{15}H_{15}ON$ α -Keto- β -*m*-toluidino- α -phenylethane (McCOMBIE and SCARBOROUGH), T., 59.
 $C_{15}H_{15}O_2N$ Phenylurethane of *d*-phenylmethylecarbinol (McKENZIE and CLOUGH), T., 697.
 $C_{15}H_{15}O_4N_3$ 3:5-Dinitro-4-benzylamino-*o*-xylene (CROSSLEY and PRATT), T., 986.
 4:6-Dinitro-3-benzylamino-*o*-xylene (CROSSLEY and PRATT), T., 988.
 4:6-Dinitro-3-*p*-toluidino-*o*-xylene (CROSSLEY and PRATT), T., 988.
 3:5-Dinitro-4-*p*-toluidino-*o*-xylene (CROSSLEY and PRATT), T., 986.
 $C_{15}H_{15}O_5N_3$ 4:6-Dinitro-3-*o*- and -*p*-anisidino-*o*-xylenes (CROSSLEY and PRATT), T., 988.
 3:5-Dinitro-4-*o*- and -*p*-anisidino-*o*-xylenes (CROSSLEY and PRATT), T., 986.
 $C_{15}H_{17}ON$ β -Hydroxy- $\alpha\beta$ -diphenylpropylamine (McKENZIE and BARROW), T., 1335.
 $C_{15}H_{17}O_7N$ 3:5-Dihydroxy-7-keto-4-dimethylaminophenyl-2-*m-p*-dihydroxyphenyl-1:4-benzopyran (WATSON and SEN), P., 349.
 $C_{15}H_{18}O_2N_4$ 1-Phenyl-2:3-dimethylpyrazolone-4-azoethyl methyl ketone (MORGAN and REILLY), T., 1499.
 Substance, from condensation of methyl acetylmethyl ketone and 1-phenyl-2:3-dimethylpyrazolone-4-diazonium chloride (MORGAN and REILLY), T., 816.
 $C_{15}H_{21}O_2N_3$ Eserine (*physostigmine*), constitution of (SALWAY), T., 351, 1988; P., 59, 287.
 $C_{15}H_{21}O_3N$ Aminoperezone, zincchloride of (REMFY), T., 1087.
 $C_{15}H_{21}O_6V$ Vanadium teracetylacetate (MORGAN and MOSS), T., 85.
 $C_{15}H_{23}O_6N$ Ethyl α -cyano- $\beta\beta$ -dimethylpropanetricarboxylate (THORPE and WOOD), T., 1533.
 $C_{15}H_{32}ON_2$ *s*-Di- δ -heptylcarbamide (PYMAN), T., 856; P., 126.

15 IV

- $C_{15}H_9O_3N_2Na$ Benzeneazocarbonylcoumaranone, sodium derivative (MERRIMAN), T., 1852.
 $C_{15}H_{15}O_4NBr$ *o*-Nitrobenzoyl derivative of 5-bromo-*o*-3-xylenol (CROSSLEY), T., 2182; P., 352.
o-Nitrobenzoyl derivatives of 5- and 6-bromo-*o*-4-xylenols (CROSSLEY and BARTLETT), T., 1299; P., 217.

15 V

$C_{15}H_{25}O_{12}N_4S_2Co$ *cis*-Sulphonyldiacetatodiethylenediaminecobaltic hydrogen sulphonyldiacetate (PRICE and BRAZIER), P., 272.

 C_{16} Group.

$C_{16}H_{10}O_8$ Diphenyl-2:5:2':5'-tetracarboxylic acid (KENNER and WITHAM), T., 238; P., 10.

$C_{16}H_{11}N$ Indenoquinoline, and its platinichloride (RUHEMANN and LEVY), T., 563.

$C_{16}H_{12}N_2$ 5:5'-Dicyano-2:2'-dimethyldiphenyl (*dicyanoditolyl*) (KENNER and WITHAM), T., 236; P., 10.

$C_{16}H_{14}O_2$ 3:5-Dibenzo- $\Delta^{3:5}$ -cycloheptadiene-1-carboxylic acid, and its barium salt (KENNER), T., 621; P., 105.

$C_{16}H_{14}O_4$ 2:2'-Dimethyldiphenyl-5:5'-dicarboxylic acid (KENNER and WITHAM), T., 236; P., 10.

$C_{16}H_{14}O_5$ Mandelic anhydride (DENHAM and WOODHOUSE), T., 1870.

$C_{16}H_{15}N$ Cinnamylidene-*p*-toluidine, and its salts (TINKLER), T., 894; P., 114.

$C_{16}H_{18}O_2$ $\alpha\beta$ -Dihydroxy- $\alpha\beta$ -di-*o*- and -*p*-tolylethanes (WREN and STILL), T., 1772; P., 262.

$C_{16}H_{18}O_3$ Benzoyl derivative of 2:2:3:3-tetramethylbicyclo[0,1,2]pentan-4-ol-5-one (FRANCIS and WILLSON), T., 2244.

$C_{16}H_{18}O_9$ Anhydride of $\beta\beta$ -dimethylpropanetricarboxylic acid (THORPE and WOOD), T., 1584.

$C_{16}H_{20}O_4$ Ethyl- α -benzylglutaconate (THORPE and WOOD), T., 1582.

$C_{16}H_{20}N_2$ Diphenyldimethylethylenediamine, and its picrate (THORPE and WOOD), T., 1609.

$C_{16}H_{22}O_6$ $\epsilon\zeta$ -Benzylidene $\beta\gamma$ -dimethyl α -methylglucoside (IRVINE and SCOTT), T., 581; P., 71.

$C_{16}H_{24}O_3$ Methylquinole of perezone (REMFY), T., 1083.

Acid, from oxidation of caulosapogenin (POWER and SALWAY), T., 201.

$C_{16}H_{24}O_6$ Gossypitol tetraethyl ether (PERKIN), T., 654; P., 110.

Quercetagetol tetraethyl ether (PERKIN), T., 216; P., 9.

$C_{16}H_{26}O_3$ Ethyl geranylacetoacetate (FORSTER and CARDWELL), T., 1345.

$C_{16}H_{32}O$ Ethyl *n*-tridecyl ketone (PICKARD and KENYON), T., 1952.

$C_{16}H_{34}O$ Ethyl-*n*-tridecylcarbinol, and its resolution and salts (PICKARD and KENYON), T., 1952.

16 III

$C_{16}H_{10}O_2Br_4$ Tetrabromo-3:5-dibenzo- $\Delta^{3:5}$ -cycloheptadiene-1-carboxylic acid (KENNER), T., 623.

$C_{16}H_{10}O_6N_4$ 2:4:5-Trinitro- α -phenylnaphthylamine (RINDL), T., 1915.

$C_{16}H_{12}O_3N_2$ *o*-, *m*-, and *p*-Toluenazocarbonylcoumaranones, and their metallic derivatives (MERRIMAN), T., 1854.

$C_{16}H_{13}ON$ 2-*o*-Aminobenzylidene-1-hydrindone (RUHEMANN and LEVY), T., 563.

$C_{16}H_{13}OCl$ 3:5-Dibenzo- $\Delta^{3:5}$ -cycloheptadiene-1-carboxylic chloride (KENNER), T., 622.

$C_{16}H_{13}O_2N$ 5-Phenyl-3-*o*-, -*m*-, and -*p*-tolyl-2:3-dihydro-2-oxazolones (McCOMBIE and SCARBOROUGH), T., 59.

$C_{16}H_{14}O_3N_2$ *o*- and *p*-Toluenehydrazocarbonylcoumaranones (MERRIMAN), T., 1854.

$C_{16}H_{14}O_4N_2$ Dibenzoyldiaminoacetic acid, and its metallic salts (HAAS), T., 1304; P., 228.

- $C_{16}H_{15}ON$ 3:6-Dibenzo- $\Delta^{3:5}$ -cycloheptadiene-1-carboxylamide (KENNER), T., 622.
- $C_{16}H_{15}ON_3$ Semicarbazones of phenyl styryl ketone, action of heat on (HEILBRON and WILSON), T., 1504; P., 245.
Substance, and its picrate from phenyl styryl ketone semicarbazones (HEILBRON and WILSON), T., 1511.
- $C_{16}H_{16}ON_2$ Hydrazide of 3:5-dibenzo- $\Delta^{3:5}$ -cycloheptadiene-1-carboxylic acid (KENNER), T., 623.
- $C_{16}H_{16}O_2N_2$ *dl*-1-Hydroxy-2-benzoylhydrazinehydrindene (PEACOCK), T., 672.
- $C_{16}H_{16}O_3N_2$ *o*-Nitrophenylacetyl- β -phenylethylamine (KAY and PICTET), T., 958; P., 131.
- $C_{16}H_{17}O_4N_3$ 6-Nitro-2-benzoylamino-4-trimethylammonium-1-benzoquinone (MELDOLA and HOLLELY), T., 180.
- $C_{16}H_{18}O_3N_4$ 1-Phenyl-2:3-dimethyl pyrazolone-4-azo acetylacetone (MORGAN and REILLY), T., 815; P., 133.
- $C_{16}H_{25}O_2N$ Camphorcarboxypiperidide, isomeric changes in (LOWRY and GLOVER), T., 913.
- $C_{16}H_{25}O_6N$ Gossypitol tetraethyl ether oxime (PERKIN), T., 655; P., 110.
Quercetagetol tetraethyl ether oxime (PERKIN), T., 216; P., 9.
- $C_{16}H_{32}O_2N_2$ α -Propylbutyryl- δ -heptylcarbamide (PYMAN), T., 860.

16 IV

- $C_{16}H_{30}OClBr$ α -Bromopalmityl chloride (HOPWOOD), P., 345.

C_{17} Group.

- $C_{17}H_{13}N_3$ 2-*p*-Tolyl-1:2-naphthatriazole (MORGAN and MICKLETHWAIT), T., 76.
- $C_{17}H_{14}O_4$ 3:5-Dibenzo- $\Delta^{3:5}$ -cycloheptadiene-1:1-dicarboxylic acid (KENNER), T., 620.
- $C_{17}H_{16}O_2$ Methyl 3:5-dibenzo- $\Delta^{3:5}$ -cycloheptadiene-1-carboxylate (KENNER), T., 622.
- $C_{17}H_{16}O_4$ Ethyl benzoylmandelate (G. M. and R. ROBINSON), P., 268.
- $C_{17}H_{16}N_2$ α -*p*-Toluidino- γ -phenylisocrotononitrile (TINKLER), T., 895; P., 114.
- $C_{17}H_{17}N_3$ 1-*p*-Tolyl-1:2:4-triaminonaphthalene (MORGAN and MICKLETHWAIT), T., 74.
- $C_{17}H_{18}O_4$ β -Keto- β -4-methoxyphenyl- α -3:4-dimethoxyphenylethane (CAIN, SIMONSEN, and SMITH), T., 1039; P., 172.
 β -Keto- α -4-methoxyphenyl- β -3:4-dimethoxyphenylethane (CAIN, SIMONSEN, and SMITH), T., 1037; P., 172.
Humulol (POWER, TUTIN, and ROGERSON), T., 1286; P., 181.
- $C_{17}H_{18}O_5$ 2:3:4:2'-Tetramethoxybenzophenone (SEN-GUPTA and WATSON), P., 270.
- $C_{17}H_{22}O_4$ Acetylpipitzol (REMFY), T., 1080.
- $C_{17}H_{22}N_2$ Diphenyldimethyltrimethylenediamine, preparation of, and its salts (THORPE and WOOD), T., 1611.
- $C_{17}H_{26}O_3$ Ethylquinole of perezone (REMFY), T., 1083.

17 III

- $C_{17}H_{12}O_4N_2$ Acetyl derivative of benzeneazocarbonylcoumaranone (MERRIMAN), T., 1852; P., 258.
- $C_{17}H_{13}ON$ 2-Phenyl-5-styryloxazole (FOULDS and ROBINSON), T., 1768; P., 261.
- $C_{17}H_{18}O_4N_3$ 2:4-Dinitro-1-*p*-tolyl- α -naphthylamine (MORGAN and MICKLETHWAIT), T., 73.

- $C_{17}H_{15}O_2N$ Styryl benzoylaminomethyl ketone (FOULDS and ROBINSON), T., 1769; P., 261.
- $C_{17}H_{15}O_5N_3$ *dl*-1-Hydroxy-2-nitropiperonylidenehydrazinohydrindene (PEACOCK), T., 674.
- $C_{17}H_{16}O_3N_2$ Ethyl phenylhydrazinocoumaranonecarboxylate (MERRIMAN), T., 1842.
dl-1-Hydroxy-2-piperonylidenehydrazinohydrindene (PEACOCK), T., 674.
- $C_{17}H_{16}O_4N_2$ Methyl dibenzoyldiaminoacetate (HAAS), T., 1306.
- $C_{17}H_{17}ON$ Acetyldibenzocycloheptadienylamine (KENNER), T., 625.
- $C_{17}H_{17}O_2N$ *apo*Morphine, attempts to synthesise (KAY and PICTET), T., 947; P., 131.
- $C_{17}H_{17}O_7I$ 3:5:7-Trihydroxy-2-*mp*-dihydroxyphenyl-4-ethyl-1:4-benzopyran anhydrohydriodide (WATSON and SEN), P., 349.
- $C_{17}H_{18}O_2N_2$ *dl*-1-Hydroxy-2-anisylidenehydrazinohydrindene (PEACOCK), T., 673.
- $C_{17}H_{18}O_2N_4$ Dihydrazide of 3:5-dibenzo- $\Delta^{3:5}$ -cycloheptadiene-1:1-dicarboxylic acid (KENNER), T., 621.
- $C_{17}H_{18}O_3N_2$ *dl*-1-Hydroxy-2-vanillylidenehydrazinohydrindene (PEACOCK), T., 674.
- $C_{17}H_{19}O_3N$ Piperine, absorption spectra of (PURVIS), T., 2293; absorption spectrum and constitution of (DOBBIE and FOX), T., 1193; P., 180.
- $C_{17}H_{19}O_4N$ Oxime of β -keto- β -4-methoxyphenyl- α -3:4-dimethoxyphenylethane (CAIN, SIMONSEN, and SMITH), T., 1039; P., 172.
 Oxime of β -keto- α -4-methoxyphenyl- β -3:4-dimethoxyphenylethane (CAIN, SIMONSEN, and SMITH), T., 1037; P., 172.
p-Methoxyphenylaceto-3:4-dimethoxyanilide (CAIN, SIMONSEN, and SMITH), T., 1037.
- $C_{17}H_{19}O_5N$ Oxime of 2:3:4:2'-tetramethoxybenzophenone (SEN-GUPTA and WATSON), P., 270.
- $C_{17}H_{20}O_2N_2$ Methyl tetrosazone (GILMOUR), P., 108.
- $C_{17}H_{20}O_4N_4$ Ethyl 1-phenyl-2:3-dimethylpyrazolone-4-azoacetoacetate (MORGAN and REILLY), T., 816; P., 133.
- $C_{17}H_{21}O_4N$ *n*- and *iso*Borneol *p*-nitrobenzoates (HENDERSON and HEILBRON), P., 381.
 Cocaine, absorption spectrum and constitution of (DOBBIE and FOX), T., 1193; P., 180.
 Hyoscyne, absorption spectrum and constitution of (DOBBIE and FOX), T., 1193; P., 180.
- $C_{17}H_{23}O_2N$ *l*-Epibornylphenylurethane (BREDT and PERKIN), T., 2223.
- $C_{17}H_{23}O_3N$ Anilic acids, from 3- and 4-methylcyclohexane-1:1-diacetic acids (THORPE and WOOD), T., 1595.
 Atropine, absorption spectra and constitution of (DOBBIE and FOX), T., 1193; P., 180.
 Hyoscyamine, absorption spectra and constitution of (DOBBIE and FOX), T., 1193; P., 180.
- $C_{17}H_{24}ON_2$ Phenylcarbamide from geranylamine (FORSTER and CARDWELL), T., 1344.
- $C_{17}H_{29}O_8N$ Triacetyl- α -aminoamylglucoside, hydrobromide of (IRVINE and HYND), T., 50.
- $C_{17}H_{35}O_2N$ Sphingosine, preparation and oxidation of (LAPWORTH), T., 1029; P., 154.

17 IV

- $C_{17}H_{18}O_2NBr$ α -Bromo- γ -phenoxybutyro-*o*-toluidide (SALWAY), T., 358.
- $C_{17}H_{23}O_3NS$ *p*-Toluenesulphonyl- β -aminocamphor (FORSTER and HOWARD), T., 66.

C₁₈ Group.

C₁₈H₂₀ 1:4-Diphenylcyclohexane (THORPE and WOOD), T., 1573.

18 II

C₁₈H₁₄O₅ Ethyl benzocoumaranonecarboxylate (MERRIMAN), T., 1843.

C₁₈H₁₆O₃ Ethyl 3:5-dibenzo- $\Delta^{3:5}$ -cycloheptadien-1-one-2-carboxylate, and its copper salt (KENNER), T., 626; P., 106.

C₁₈H₁₈O₂ Ethyl 3:5-dibenzo- $\Delta^{3:5}$ -cycloheptadiene-1-carboxylate (KENNER), T., 622.

C₁₈H₁₈O₄ Dimethyl 2:2'-ditolyl-5:5'-dicarboxylate (KENNER and WITHAM), T., 237; P., 10.

C₁₈H₂₄N₂ Diphenyldiethylethylenediamine, and its dipicrate (THORPE and WOOD), T., 1608.

C₁₈H₂₈O₃ Propylquinole of perezone (REMFREY), T., 1084.

C₁₈H₂₈O₈ Ethyl dicarbethoxydimethylcyclopropane, structure of lactones from (PERKIN and THORPE), T., 1760; P., 259.

C₁₈H₃₂O₂ Chaulmoogric acid, in the seeds of *Oncoba echinata* (GOULDING and AKERS), P., 197.

C₁₈H₃₆O Ethyl *n*-pentadecyl ketone (PICKARD and KENYON), T., 1953.

C₁₈H₃₆O Ethyl-*n*-pentadecylcarbinol, and its resolution and salts (PICKARD and KENYON) T., 1953.

18 III

C₁₈H₁₁O₈N Nitro-2:7-diacetoxypheanthraquinone (MUKERJEE and WATSON), P., 268.

C₁₈H₁₃O₃N₅ *p*-Nitrobenzeneazobenzeneazophenol (POPE and WILLETT), T., 1261; P., 191.

C₁₈H₁₄O₄N₂ Acetyl derivatives of *o*-, *m*-, and *p*-tolueneazocarbonylcoumarones (MERRIMAN), T., 1854.

2:7-Diacetylaminophenanthraquinone (MUKERJEE and WATSON), P., 269.

C₁₈H₁₅O₂N 3-Hydroxy-2:5-diphenyl-6-methyl-1:2-dihydropyridone (THORPE and WOOD), T., 1577.

C₁₈H₁₇O₃N Semianilide of β -phenyl- α -methylglutaconic acid (THORPE and WOOD), T., 1577.

C₁₈H₁₈ON₂ *dl*-1-Hydroxy-2-cinnamylidenehydrazinohydrindene (PEACOCK), T., 674.

C₁₈H₁₈O₂N₂ 1:3-Dibenzoylhexahydropyrimidine (TITHERLEY and BRANCH), T., 339; P., 29.

C₁₈H₁₈O₄N₂ Ethyldibenzoyldiaminoacetate (HAAS), T., 1306.

Substance, from dehydration of 2-nitrohomoveratroyl- β -phenylethylamine (KAY and PICTET), T., 957; P., 131.

C₁₈H₁₉ON Benzoyl derivatives of 4:6- and -4:7-dimethyl-1:2:3:4-tetrahydroquinolines (EWINS and KING), T., 110.

Benzoyl derivative of 4:8-dimethyl-1:2:3:4-tetrahydroquinoline (EWINS and KING), T., 109.

Benzoyl derivative of α -cytisolidine (EWINS), T., 104.

C₁₈H₁₉O₂N 3:5-Dibenzo- $\Delta^{3:5}$ -cycloheptadienylurethane (KENNER), T., 624; P., 105.

C₁₈H₂₀O₄Sn Substance, from the action of benzyl acetate on dibenzylstannic oxide (SMITH and KIPPING), T., 2048.

C₁₈H₂₀O₅N₂ 2-Nitrohomoveratroyl- β -phenylethylamine (KAY and PICTET), T., 957; P., 131.

C₁₈H₂₁O₃N Benzoylbornylene-3-hydroxamic acid (BREDT and PERKIN), T., 2205.

- $C_{18}H_{22}O_3N_2$ Methyl tetrosephenylbenzylhydrazone (GILMOUR), P., 363.
 $C_{18}H_{36}O_3N_2$ α -Aminopalmitylglycine (HOPWOOD), P., 345.

18 IV

- $C_{18}H_{13}O_2N_2Cl$ 5-*p*-Chlorobenzeneazo-2:2'-diphenol (ROBERTSON and BRADY), T., 1483.
 $C_{18}H_{34}O_3NBr$ α -Bromopalmitylglycine (HOPWOOD), P., 345.

18 V

- $C_{18}H_{10}O_2N_2ClBr_3$ 5-*p*-Chloro-3:3':5'-tribromobenzeneazo-2:2'-diphenol (ROBERTSON and BRADY), T., 1483.

 C_{19} Group.

- $C_{19}H_{12}O_3$ Resoreinol-benzein (3-hydroxy-9-phenylfluorone) (POPE), P., 378.
 $C_{19}H_{14}O_4$ 3:4-Diphenyl- $\Delta^{3:4}$ -cyclopentenone-2-oxalic acid (RUHEMANN and LEVY), T., 557.
 $C_{19}H_{16}O_4$ Cotarnonideneacetophenone (*phenyl 2-methoxy-3:4-methylenedioxy-6-vinylstyryl ketone*) (HOPE and ROBINSON), T., 372.
 $C_{19}H_{16}O_5$ 2-Methoxy-3:4-methylenedioxy-6-vinyl- α -phenylcinnamic acid (HOPE and ROBINSON), T., 368.
 $C_{19}H_{24}O_6$ Ethyl α -carbethoxy- β -phenyl- α -methylglutaconate (THORPE and WOOD), T., 1574.
 $C_{19}H_{26}N_2$ Diphenyldiethyltrimethylenediamine, and its picrate (THORPE and WOOD), T., 1610.
 8-Diphenylheptamethylenediamine, and its hydrochloride (LE SUEUR), T., 1125.
 $C_{19}H_{28}O$ Homogeranyphenylmethylcarbinol (FORSTER and CARDWELL), T., 1346.

19 III

- $C_{19}H_{15}O_2N$ 5-Phenyl-3- β -naphthyl-2:3-dihydro-2-oxazolone (McCOMBIE and SCARBOROUGH), T., 60.
 $C_{19}H_{13}O_2Br_3$ Ketohydrindylmethyleneketobromohydrindene dibromide (RUHEMANN and LEVY), T., 555; P., 74.
 $C_{19}H_{14}O_2N_4$ *p*-Nitrobenzylideneaminoazobenzene (POPE and WILLETT), T., 1259.
 $C_{19}H_{15}ON_3$ *p*-Hydroxybenzylideneaminoazobenzene (POPE and WILLETT), T., 1258.
 $C_{19}H_{15}O_2N_3$ 2:4-Dihydroxybenzylideneaminoazobenzene (POPE and WILLETT), T., 1259.
 $C_{19}H_{17}ON_3$ Substance, from 1-*p*-tolyl-1:2:4-triaminonaphthalene and nitrosyl sulphate (MORGAN and MICKLETHWAIT), T., 76.
 $C_{19}H_{17}O_3Br$ Benzoyl derivative of 1-bromo-2:2:3:3-tetramethylbicyclo[0,1,2,]pentan-4-ol-5-one (FRANCIS and WILLSON), T., 2242.
 $C_{19}H_{13}O_4N_4$ 6-Nitro-2- β -naphtholazo-4-trimethylammonium-1-benzoquinone (+ H_2O), and its chloride (MELDOLA and HOLLELY), T., 189.
 $C_{19}H_{23}O_9N$ Triacetyl- α -amino-*o*-aldehydophenylglucoside, hydrobromide of (IRVINE and HYND), T., 51.
 $C_{19}H_{25}O_2N_2$ α -Dimethylamino- γ -phenoxybutyro-*o*-toluidide, and its salts (SALWAY), T., 358.
 $C_{19}H_{24}O_4N_4$ ζ -Monomethylglucosazone (IRVINE and SCOTT), T., 573.
 $C_{19}H_{25}O_8N$ Triacetyl- α -aminobenzylglucoside, hydrobromide of (IRVINE and HYND), T., 51.

C₂₀ Group.

- C₂₀H₁₂O₇ Hydroxyquinol-phthalein anhydride (GHOSH and WATSON), P., 9.
- C₂₀H₁₄O₄ Phenolphthalein, constitution of, and its alkali salts (FORT and BARRETT), P., 270.
- C₂₀H₁₈O₄ Tetramethyl diphenyl-2:5:2':5'-tetracarboxylate (KENNER and WITHAM), T., 237; P., 10.
- C₂₀H₂₀O₇ Methylquercetin tetramethyl ether (PERKIN), T., 1635; P., 253.
- C₂₀H₂₀O₈ Quercetagenin pentamethyl ether (PERKIN), T., 213; P., 9.
- C₂₀H₂₂O₄ Diacetyl derivatives of $\alpha\beta$ -dihydroxy- $\alpha\beta$ -di-*o*- and -*p*-tolylethanes (WREN and STILL), T., 1772; P., 262.
- Diethyl 2:2'-dimethyldiphenyl-5:5'-dicarboxylate (KENNER and WITHAM), T., 237; P., 10.
- Diethyl 2:2'-dimethyldiphenyl- $\omega\omega'$ -dicarboxylate (KENNER), T., 625; P., 106.
- C₂₀H₂₈N₂ 3-Diphenyloctamethylenediamine, and its hydrochloride (LE SUEUR), T., 1121.

20 III

- C₂₀H₁₀O₆N₄ 2:4:2':4'-Tetranitro- $\alpha\alpha$ -dinaphthyl (RINDL), T., 1917.
- C₂₀H₁₂OS Naphthathioxin, constitution of (NOLAN and SMILES), T., 901; P., 151.
- iso*Naphthathioxin (NOLAN and SMILES), T., 347, 903; P., 53, 151.
- C₂₀H₁₂O₂S *iso*Naphthathioxin oxide (NOLAN and SMILES), T., 910.
- C₂₀H₁₂O₃S Naphthathioxin dioxide (NOLAN and SMILES), T., 908.
- iso*Naphthathioxin dioxide (NOLAN and SMILES), T., 912.
- C₂₀H₁₂O₆N₄ 3:3'-Dinitrophthalylbenzidine (CAIN, COULTHARD, and MICKLETHWAIT), T., 2078.
- C₂₀H₁₄O₂S β -Naphthol sulphides, constitution of (NOLAN and SMILES), P., 197.
- C₂₀H₁₄O₂N₄ 3:3'- and 3:5'-Dinitro-4:4'-disucciniminodiphenyl (CAIN, COULTHARD, and MICKLETHWAIT), T., 2078.
- C₂₀H₁₅O₂N₃ Diphenylcarbamylo-, -*m*-, and -*p*-nitrobenzsynaldoximes (BRADY and DUNN), T., 1617.
- C₂₀H₁₆O₂N₂ Diphenylcarbamybenzsynaldoxime (BRADY and DUNN), T., 1616.
- C₂₀H₁₇ON₃ *p*-Methoxybenzylideneaminoazobenzene (POPE and WILLETT), T., 1259.
- C₂₀N₁₈O₂N₂ Anhydrocotarnineisatin (HOPE and ROBINSON), T., 376.
- C₂₀H₁₈O₅V Vanadium oxybisbenzoylacetate (MORGAN and MOSS), T., 87.
- C₂₀H₁₉ON β -Hydroxy- $\alpha\beta\beta$ -triphenylethylamine (McKENZIE and BARROW), T., 1336.
- C₂₀H₂₀O₃N₂ Anil-anilide from $\beta\beta$ -dimethylpropanetricarboxylic acid (THORPE and WOOD), T., 1585.
- Anhydrocotarninephenylacetonitrile (HOPE and ROBINSON), T., 366.
- C₂₀H₂₁O₄N Anhydrocotarnineacetophenone, and its salts (HOPE and ROBINSON), T., 369; P., 63.
- C₂₀H₂₂O₂N₂ 1:4-Dibenzoyl-2- and -3-dimethylpiperazines, absorption spectra of (PURVIS), T., 2287.
- C₂₀H₂₅ON Tetrahydroquinolino-*d*- and -*dl*-methylenecamphors (POPE and READ), T., 1529.
- C₂₀H₂₅O₂N *d*- and *l*-Hydroxyhydrindamino-*d*-methylenecamphor (POPE and READ), T., 447.

20 IV

- $C_{20}H_8O_9N_4Cl_4$ (3:4:5:6-Tetrachloro)phthalyl-3:3'- and -3:5'-dinitrobenz-idines (CAIN, COULTHARD, and MICKLETHWAIT), T., 2079.
 $C_{20}H_{10}OCl_2S$ Dichloronaphthathioxin (NOLAN and SMILES), T., 907.
 $C_{20}H_{10}OBr_2S$ Dibromonaphthathioxin (NOLAN and SMILES), T., 908.
 Dibromoisonaphthathioxin (NOLAN and SMILES), T., 349; P., 53.

 C_{21} Group.

- $C_{21}H_{15}N_3$ Cyaphenine, constitution of (MACKENZIE), P., 175.
 $C_{21}H_{18}O_4$ Ethyl 3:4-diphenyl- $\Delta^{3:4}$ -cyclopentenone-2-oxalate (RUHEMANN and LEVY), T., 557.
 $C_{21}H_{20}O_2$ $\alpha\beta$ - and $\alpha\gamma$ -Dihydroxy- $\alpha\alpha\gamma$ -triphenylpropanes, optically active (MCKENZIE and MARTIN), T., 113.
 $C_{21}H_{22}O_4$ Diethyl 3:5-dibenzo- $\Delta^{3:5}$ -cycloheptadiene-1:1-dicarboxylate (KENNER), T., 621.
 $C_{21}H_{22}O_7$ Methylquercetin pentamethyl ether (PERKIN), T., 1634; P., 253.
 $C_{21}H_{22}O_8$ Gossypetin hexamethyl ether (PERKIN), T., 653; P., 110.
 Quercetagetin hexamethyl ether (PERKIN), T., 214; P., 9.
 $C_{21}H_{33}N$ *d*-, *n*-, and *neo*-Bornylamino-*d*-methylenecamphor (POPE and READ), T., 456.

21 III

- $C_{21}H_{16}ON_2$ 1:3:4-Triphenyl-2:3-dihydro-2-glyoxaline, and its picrate (McCOMBIE and SCARBOROUGH), T., 60.
 $C_{21}H_{16}N_2S$ 1:3:4-Triphenyl-2:3-dihydro-2-glyoxalthione (McCOMBIE and SCARBOROUGH), T., 62.
 $C_{21}H_{17}O_2N$ Benzodesylamide (MCKENZIE and BARROW), T., 1334.
 3:4:5-Triphenyl-2:3:4:5-tetrahydro-2-oxazolone (CROWTHER and McCOMBIE), T., 29.
 $C_{21}H_{19}ON_5$ 1-Phenyl-2:3-dimethylpyrazolone-4-azo- β -naphthylamine, and its hydrochloride (MORGAN and REILLY), T., 814; P., 133.
 $C_{21}H_{19}O_2N$ 4:5-Diphenyl-3- β -naphthyl-2:3:4:5-tetrahydro-2-oxazolone (CROWTHER and McCOMBIE), T., 31.
 $C_{21}H_{19}O_5N$ Anhydrocotarnine-1:3-diketohydrindene (HOPE and ROBINSON), T., 374.
 $C_{21}H_{20}O_3N_4$ 1-Phenyl-2:3-dimethylpyrazolone-4-azobenzoylacetone (MORGAN and REILLY), T., 1496.
 $C_{21}H_{21}ON$ α -Hydroxy- β -*m*-toluidino- $\alpha\beta$ -diphenylethane (CROWTHER and McCOMBIE), T., 29.
 $C_{21}H_{21}O_3N$ Anhydrocotarnineindene, and its salts (HOPE and ROBINSON), T., 375.
 $C_{21}H_{21}O_4N$ Anhydrocotarnine-1-hydrindone (HOPE and ROBINSON), T., 374.
 $C_{21}H_{22}O_3N_2$ Anhydrocotarnine- α -methylindole (HOPE and ROBINSON), T., 376.
 Methylanhydrocotarninephenylacetonitrile, and its picrate (HOPE and ROBINSON), T., 366.
 $C_{21}H_{23}O_4N$ Anhydromethylcanadines, and their salts (PYMAN), T., 833; P., 125.
 Base, from *l*-canadine methohaloids (JOWETT and PYMAN), T., 299.
 $C_{21}H_{23}O_5N$ γ -Homochelidonine (+ $\frac{1}{2}$ EtOH) (JOWETT and PYMAN), T., 299; P., 26.
 $C_{21}H_{26}O_4N_2$ $\alpha\eta$ -Dianilinoazelaic acid (LE SUEUR), T., 1124.

- $C_{21}H_{27}ON$ Tetrahydroquinaldinomethylenecamphors, stereoisomeric (POPE and READ), T., 1515; P., 247.
 $C_{21}H_{27}O_6N$ Ethyl α -cyano- γ -benzylisobutane- $\alpha\gamma\gamma'$ -tricarboxylate (THORPE and WOOD), T., 1582.
 $C_{21}H_{33}ON$ *d*- α -Camphylamino-*d*- and -*l*-methylenecamphor (POPE and READ), T., 453.

21 IV

- $C_{21}H_{15}O_2N_4Na$ Benzeneazocarbonylcoumaranonephenylhydrazone, sodium derivative (MERRIMAN), T., 1853.
 $C_{21}H_{19}O_4N_5S$ 1-Phenyl-2:3-dimethylpyrazolone-4-(1')-azo- β -naphthylamine-6'-sulphonic acid (MORGAN and REILLY), T., 1501.
 $C_{21}H_{20}O_4NCl$ 2:3:4:2'-Tetrahydroxy-4''-dimethylaminotriphenylcarbinol anhydro-hydrochloride (SEN-GUPTA and WATSON), P., 269.
 $C_{21}H_{24}O_4NCl$ Tetrahydroberberine methochlorides, and the constitution of anhydro bases derived from them (PYMAN), T., 825; P., 125.
l- α - and - β -Canadine methochlorides (JOWETT and PYMAN), T., 296; P., 26.
 $C_{21}H_{24}O_4NI$ Tetrahydroberberine methiodides, and the constitution of anhydrobases derived from them (PYMAN), T., 825; P., 125.
l- α - and - β -Canadine methiodides (JOWETT and PYMAN), T., 296; P., 26.

C_{22} Group.

- $C_{22}H_{24}O_3$ Substance, from condensation of phenol and camphorquinone (SEN-GUPTA and DEV), P., 155.
 $C_{22}H_{24}O_4$ Benzoylpipitzol (REMFREY), T., 1081.
 $C_{22}H_{41}O_2$ Methyl cluytinate (POWER, TUTIN, and ROGERSON), T., 1284.

22 III

- $C_{22}H_{14}O_4S_2$ Anhydride, from sulphur chloride and silver α -naphthoate (DENHAM and WOODHOUSE), T., 1866.
 $C_{22}H_{16}O_2N_2$ 5-Naphthaleneazo-2:2'-diphenol (ROBERTSON and BRADY), T., 1484.
 $C_{22}H_{16}O_8N_2$ $\alpha\delta$ -Diphthaliminoadipic acid (STEPHEN and WEIZMANN), T., 273.
 $C_{22}H_{18}N_2O_2$ 3:4-Diphenyl-1-*o*-, -*m*-, and -*p*-tolyl-2:3-dihydro-2-glyoxalones, and their picrates (McCOMBIE and SCARBOROUGH), T., 61.
 $C_{22}H_{18}O_2S$ β -Naphthol sulphide dimethyl ether (NOLAN and SMILES), T., 345.
 $C_{22}H_{18}N_2S$ 3:4-Diphenyl-1-*o*-, -*m*-, and -*p*-tolyl-2:3-dihydro-2-glyoxalthiones (McCOMBIE and SCARBOROUGH), T., 62.
 $C_{22}H_{19}ON_3$ Phenylsemicarbazones of phenyl styryl ketone (HEILBRON and WILSON), T., 1512.
 $C_{22}H_{20}O_{10}N_2$ $\alpha\delta$ -Diphthalaminoadipic acid (+ 2H₂O) (STEPHEN and WEIZMANN), T., 274.
 $C_{22}H_{26}O_{11}N_2$ Substance, and its silver salt, from the action of nitric acid on aconitine (BRADY), T., 1825.
 $C_{22}H_{28}O_4N_2$ $\alpha\theta$ -Dianilinosebacic acid (LE SUEUR), T., 1120.
 $C_{22}H_{30}O_2N_2$ Di-*d*-bornylene-3-carboxylic hydrazide (BREDT and PERKIN), T., 2201.

22 IV

- $C_{22}H_{22}O_8N_8Cr_2$ 1-Phenyl-2:3-dimethylpyrazolone-4-diazonium dichromate, and its hydrochloride (MORGAN and REILLY), T., 812.
 $C_{22}H_{23}O_8N_8Cl_3$ 1-Phenyl-2:3-dimethylpyrazolone-4-diazonium chloride, and its platinichloride (MORGAN and REILLY), T., 812; P., 133.

C₂₃ Group.

- C₂₃H₁₄O₂** Phenylenedibenzospiropyran (RUHEMANN and LEVY), T., 562.
C₂₃H₁₇N₃ 2:3-Diphenyl-2:3-dihydro-1:3:4-naphthaisotriazine, resolution of, into its optically active components and preparation of its salts (POPE and TAYLOR), T., 1763; P., 259.
C₂₃H₁₈O Anhydride of β -1:1-dihydroxydinaphthylpropane (SEN-GUPTA), P., 382.
C₂₃H₂₄O₂ *d*- $\beta\gamma$ - and *l*- $\beta\delta$ -Dihydroxy- $\alpha\delta$ -diphenyl- β -benzyl-*n*-butanes (McKENZIE and MARTIN), T., 116.
C₂₃H₂₄O₄ Phenylhydrazone of 2:3:4:2'-tetramethoxybenzophenone (SEN-GUPTA and WATSON), P., 270.
C₂₃H₃₂O₁₅ Acetyl derivative from methylated cellulose (DENHAM and WOODHOUSE), T., 1741.
C₂₃H₄₀O₂ Acid, from oxidation of oleanone (TUTIN and NAUNTON), T., 2059.

23 III

- C₂₃H₁₈O₂N₄** Acetyl derivative of benzeneazocarbonylcoumaranonephenylhydrazone (MERRIMAN), T., 1853.
C₂₃H₂₀O₂N₄ *o*- and *p*-Tolueneazocarbonylcoumaranone-*p*-tolylhydrazones (MERRIMAN), T., 1855.
C₂₃H₂₃ON₅ 1-Phenyl-2:3-dimethylpyrazolone-4-azoethyl- β -naphthylamine, and its hydrochloride (MORGAN and REILLY), T., 1500.
C₂₃H₂₃O₃N α -Ethylcarbonato- β -anilino- $\alpha\beta$ -diphenylethane (CROWTHER and McCOMBIE), T., 29.
C₂₃H₂₆O₄N₂ Brucine, salt of, with methyl tetronic acid (GILMOUR), P., 363.
C₂₃H₂₇O₅N Ethyl anhydrocotarninephenylacetate, and its salts (HOPE and ROBINSON), T., 367.
C₂₃H₃₀O₂N₂ *s*-Diacetyldiphenylheptamethylenediamine (LE SUEUR), T., 1126.
C₂₃H₃₀O₂N₂ α -Aminomorphineglucoside, and its hydrochloride (IRVINE and HYND), T., 55.

C₂₄ Group.

- C₂₄H₁₆O₃** Substance, from oxidation of β -1:1-dihydroxydinaphthylpropane (SEN-GUPTA), P., 382.
C₂₄H₁₆O₄ Substance, from oxidation of β -1:1-dihydroxydinaphthylpropane (SEN-GUPTA), P., 382.
C₂₄H₁₈O₃ Dihydroxy-derivative from substance, **C₂₄H₁₆O₄** (SEN-GUPTA), P., 382.
C₂₄H₂₀O Anhydride of 1:1-dihydroxymethylethyl- $\alpha\alpha$ -dinaphthylmethane (SEN-GUPTA), P., 28.

24 III

- C₂₄H₁₄O₁₀N₄** Tetranitro-4'':4'''-dihydroxybenzerythrene (CAIN, COULTHARD, and MICKLETHWAIT), T., 2084.
C₂₄H₁₆O₆N₆ 3:3'- and 3:5'-Dinitrodiphenyl-4:4'-bisazophenols (CAIN, COULTHARD, and MICKLETHWAIT), T., 2079.
C₂₄H₁₈O₂N₄ 5:5'-Bisbenzeneazo-2:2'-diphenol (+ $\frac{1}{2}$ H₂O), and its hydrochloride (ROBERTSON and BRADY), T., 1482; P., 248.
C₂₄H₁₈O₄N₄ 5:5'-Bis-*p*-hydroxybenzeneazo-2:2'-diphenol (ROBERTSON and BRADY), T., 1484.
C₂₄H₁₆O₄S Diacetyl derivative of unstable β -naphthol sulphide (NOLAN and SMILES), T., 347.
C₂₄H₁₉O₂N 4:5-Diphenyl-3-*m*- and -*p*-tolyl-2:3:4:5-tetrahydro-2-oxazolones (CROWTHER and McCOMBIE), T., 30.

- $C_{24}H_{21}ON$ β -Hydroxy- $\alpha\beta$ -diphenyl- β -naphthylethylamine (McKENZIE and BARROW), T., 1335.
 α -Hydroxy- β -2-naphthylamino- $\alpha\beta$ -diphenylethane (CROWTHER and McCOMBIE), T., 30.
 $C_{24}H_{29}O_2N$ Substance, from oxidation of aconitine (BRADY), T., 1824.
 $C_{24}H_{32}O_2N_2$ *s*-Diacetyldiphenyloctamethylenediamine (LE SUEUR), T., 1121.
 $C_{24}H_{41}O_2N$ α -Anilinostearic acid, resolution of (LE SUEUR), T., 2108; P., 306.

24 IV

- $C_{24}H_{12}O_8N_4Cl_2$ 4'':4'''-Dichlorotetranitrobenzerythrene (CAIN, COULTHARD, and MICKLETHWAIT), T., 2080.
 $C_{24}H_{12}O_8N_4Br_2$ 4'':4'''-Dibromotetranitrobenzerythrene (CAIN, COULTHARD, and MICKLETHWAIT), T., 2082.
 $C_{24}H_{16}O_2N_4Cl_2$ 5:5'-Bis-*o*- and -*p*-chlorobenzeneazo-2:2'-diphenol (ROBERTSON and BRADY), T., 1483.
 $C_{24}H_{16}O_2N_4Br_2$ 3:3'-Dibromo-5:5'-bisbenzeneazo-2:2'-diphenol (ROBERTSON and BRADY), T., 1482.

C_{25} Group.

- $C_{25}H_{22}O$ Anhydride of γ -1:1-dihydroxydinaphthylpentane (SEN-GUPTA), P., 382.
 Substance, from methyl propyl ketone or diethyl ketone and α -naphthol (SEN-GUPTA), P., 30.

25 III

- $C_{25}H_{18}ON_2$ 3:4-Diphenyl-1- β -naphthyl-2:3-dihydro-2-glyoxalone, and its picrate (McCOMBIE and SCARBOROUGH), T., 62.
 $C_{25}H_{26}O_2N_2$ Phenyl- β -naphthylbenzoylmethylcarbamide (McCOMBIE and SCARBOROUGH), T., 61.
 $C_{25}H_{23}O_3N$ Anhydrocotarninefluorene, and its picrate (HOPE and ROBINSON), T., 375.

C_{26} Group.

- $C_{26}H_{12}O_8N_6$ 4'':4'''-Dicyanotetranitrobenzerythrene (CAIN, COUTHARD, and MICKLETHWAIT), T., 2082.
 $C_{26}H_{16}O_4N_4$ Phenanthraquinone-2:7-bisazophenol (MUKERJEE and WATSON), P., 269.
 $C_{26}H_{18}O_6N_4$ Dibenzoyl-3:3' and -3:5'-dinitrobenzidines (CAIN, COULTHARD, and MICKLETHWAIT), T., 2077.
 $C_{26}H_{22}O_2N_4$ 5:5'-Bis-*p*-tolueneazo-2:2'-diphenol(+ $\frac{1}{2}H_2O$) (ROBERTSON and BRADY), T., 1482.
 $C_{26}H_{24}O_8N_2$ Ethyl $\alpha\delta$ -diphthaliminoadipate (STEPHEN and WEIZMANN), T., 273.
 $C_{26}H_{27}O_3N_3$ Trianilide from $\beta\beta$ -dimethylpropanetricarboxylic acid (THORPE and WOOD), T., 1585.

26 IV

- $C_{26}H_{12}O_8N_6S_2$ Tetranitro-4'':4'''-dithiocyanobenzerythrene (CAIN, COULTHARD, and MICKLETHWAIT), T., 2083.

C₂₇ Group.

- C₂₇H₂₂O** Substance, from benzophenone and α -naphthol (SEN-GUPTA), P., 30.
C₂₇H₃₀O₁₆ Kaempferin (+ 6H₂O) (TUTIN), T., 2012; P., 278.
C₂₇H₃₄O₈ Gossypetin hexaethyl ether (PERKIN), T., 654; P., 110.
 Quercetagetin hexaethyl ether (PERKIN), T., 214; P., 9.

27 III

- C₂₇H₂₂ON₄** Substance, and its hydrochloride from diazodeoxybenzoin and magnesium phenyl bromide (FORSTER and CARDWELL), T., 868; P., 150.
C₂₇H₂₄O₂N₂ 5-*p*-Diethylaminoanilo-3:4-diphenyl- $\Delta^{3:4}$ -cyclopentene-1:2-dione, and its platinichloride (RUHEMANN and LEVY), T., 561.
C₂₇H₂₅O₅N Benzoylanhydrocotarnineacetophenone (HOPE and ROBINSON), T., 369.
C₂₇H₂₅O₆N Benzoylanhydrocotarninephenylacetic acid (HOPE and ROBINSON), T., 365.
C₂₇H₃₇O₇I 3:5:7-Triethoxy-2-*mp*-diethoxyphenyl-4-ethyl-1:4-benzopyran anhydrohydriodide (WATSON and SEN), P., 349.

C₂₈ Group.

- C₂₈H₂₀O** Substance, from acetophenone and α -naphthol (SEN-GUPTA), P., 30.
C₂₈H₂₀O₁₁ Acetyl derivative of hydroxyquinolphthalein anhydride (GHOSH and WATSON), P., 10.
C₂₈H₃₂O₈ Substance, from condensation of $\omega\omega'$ -dibromo-2:2'-ditolyl and tetraethyl ethanetetracarboxylate (KENNER), T., 626.
C₂₈H₃₂N₂ 3-Di-1- and -2-naphthyl octamethylenediamines, and hydrochloride of the latter (LE SUEUR), T., 1122.

28 III

- C₂₈H₁₄O₈N₄** 4:4'-Diphthalimino-3:5'-dinitrodiphenyl (CAIN, COULTHARD, and MICKLETHWAIT), T., 2078.
C₂₈H₃₈O₄N₂ Cephæline, hydrochlorides from (CARR and PYMAN), P., 227.

28 IV

- C₂₈H₁₂O₈N₄Cl₄** 4:4'-Di(3:6-dichloro)-phthalimino-3:3'- and -3:5'-dinitrodiphenyl (CAIN, COULTHARD, and MICKLETHWAIT), T., 2079.

C₂₉ Group.

- C₂₉H₄₂O₄** Substances, from oxidation of oleanone with chromic acid (TUTIN and NAUNTON), T., 2058; P., 301.
C₂₉H₄₆O₄ Oleanone (TUTIN and NAUNTON), T., 2054; P., 301.
C₂₉H₅₀O₅ Ipuranol, constitution of (POWER and SALWAY), T., 399; P., 63.
C₂₉H₅₀O₂₀ Substance, from methylation of cellulose (DENHAM and WOODHOUSE), T., 1739; P., 251.

29 III

- C₂₉H₂₄O₂N₄** Acetyl derivative of substance, from diazodeoxybenzoin and magnesium phenyl bromide (FORSTER and CARDWELL), T., 869.
C₂₉H₃₂O₄N₂ Rubremetine, hydrochloride of (CARR and PYMAN), P., 227.

C₃₀ Group.

- C₃₀H₃₀O₈N₂** $\omega\omega'$ -Diphthalimino-2:2'-dimethyldiphenyl (KENNER), T., 627.
C₃₀H₂₇O₆V Vanadium terbenzoylacetate (MORGAN and MOSS), T., 87.
C₃₀H₃₂O₄N₂ $\alpha\theta$ -Di-1- and -2-naphthylaminosebacic acids (LE SUEUR), T., 1122.

C₃₁ Group.

- C₃₁H₁₈O₂ Phenylenedi- β -naphthaspiropyran (RUHEMANN and LEVY), T., 563.
 C₃₁H₂₀O₂ 3:3'-Diphenylacetylenedibenzospiro pyran (RUHEMANN and LEVY), T., 559.
 C₃₁H₂₂O 3:4-Diphenyl-2:5-dibenzylidene- $\Delta^{3:4}$ -cyclopentenone (RUHEMANN and LEVY), T., 557.
 C₃₁H₄₄O₅ Acetyl derivatives of substances C₂₉H₄₂O₄ (TUTIN and NAUNTON), T., 2058; P., 301.
 C₃₁H₄₈O₅ Acetyloleanone (TUTIN and NAUNTON), T., 2055; P., 301.

31 III

- C₃₁H₂₀O₅N₂ 3:4-Diphenyl-2:5-di-*p*-nitrobenzylidene- $\Delta^{3:4}$ -cyclopentenone (RUHEMANN and LEVY), T., 558.

31 IV

- C₃₁H₃₄O₄N₂S₂ *s*-Dibenzenesulphonyldiphenylheptamethylenediamine (LE SUEUR), T., 1126.

C₃₂ Group.

- C₃₂H₂₀O₆N₆ 3:3'- and 3:5'-Dinitrodiphenyl-4:4'-bisazo- β -naphthols (CAIN, COULTHARD, and MICKLETHWAIT), T., 2080.
 C₃₂H₆₂O₄S₂ Anhydride, from sulphur chloride and silver palmitate (DENHAM and WOODHOUSE), T., 1866.

32 IV

- C₃₂H₃₆O₄N₂S₂ *s*-Dibenzenesulphonyldiphenyloctamethylenediamine (LE SUEUR), T., 1121.

C₃₃ Group.

- C₃₃H₂₂O₈ Tetrabenzoylmethyltetritol (GILMOUR), P., 363.
 C₃₃H₅₀O₆ Diacetyloleanone (TUTIN and NAUNTON), T., 2055; P., 301.
 C₃₃H₅₆O₆ Cholesterol-*d*-glucoside (SALWAY), T., 1024; P., 170.
 Sitosterol-*d*-glucoside (SALWAY), T., 1042; P., 170.
 C₃₃H₆₆O₆ Ceryl-*d*-glucoside (SALWAY), T., 1027; P., 171.

C₃₄ Group.

- C₃₄H₃₈O₁₀ Pinacone from 2:3:4:2'-tetramethoxybenzophenone (SEN-GUPTA and WATSON), P., 270.

34 III

- C₃₄H₂₄O₃N₈ Substance, from 1-*p*-tolyl-1:2:4-triaminonaphthalene and nitrosyl sulphate (MORGAN and MICKLETHWAIT), T., 76.
 C₃₄H₄₀O₄N₂ Ethyl $\alpha\theta$ -di-1-, and -2-naphthylaminosebacates (LE SUEUR), T., 1122.
 C₃₄H₄₇O₁₁N Aconitine, constitution of, and its chromate (BRADY), T., 1821; P., 253.

C₃₅ Group.

- C₃₅H₂₆O 3:4-Diphenyl-2:5-dieinnamyliidene- $\Delta^{3:4}$ -cyclopentenone (RUHEMANN and LEVY), T., 558.

35 III

$C_{35}H_{57}O_{13}N_{11}$ Gelatin, swelling of, with dilute acids (PROCTER), P., 370.

 C_{36} Group.

$C_{36}H_{72}O_6$ Myricyl-*d*-glucoside (SALWAY), T., 1027 ; P., 171.

 C_{38} Group.

$C_{38}H_{24}O_{11}$ Hydroxyquinol-benzein (GHOSH and WATSON), P., 10.

 C_{39} Group.

$C_{39}H_{24}O_2$ Diphenylacetylenedi- β -naphthaspiropyran (RUHEMANN and LEVY), T., 560.

 C_{41} Group.

$C_{41}H_{64}O_{10}$ Tetra-acetylcholesterol-*d*-glucoside (SALWAY), T., 1025.

Tetra-acetylsitosterol-*d*-glucoside (SALWAY), T., 1025.

$C_{41}H_{74}O_{10}$ Tetra-acetylceeryl-*d*-glucoside (SALWAY), T., 1029.

 C_{42} Group.

$C_{42}H_{66}O_6$ Caulosapogenin (POWER and SALWAY), T., 198 ; P., 2.

42 III

$C_{42}H_{44}O_4Si_2$ Dianhydrotris(dibenzylsilicanediol (ROBISON and KIPPING), P., 348.

$C_{42}H_{44}O_4Sn_3$ Dianhydrotris(dibenzylstannanediol (SMITH and KIPPING), T., 2041 ; P., 280.

 C_{43} Group.

$C_{43}H_{26}O_{10}$ Tetrabenzoylkaempferol (TUTIN), T., 2010.

$C_{43}H_{64}O_{27}$ Acetyl derivative from methylated cellulose (DENHAM and WOODHOUSE), T., 1741.

$C_{43}H_{68}O_6$ Caulosapogenin monomethyl ether (POWER and SALWAY), T., 200.

 C_{44} Group.

$C_{44}H_{80}O_{10}$ Tetra-acetylmyricyl-*d*-glucoside (SALWAY), T., 1027.

 C_{46} Group.

$C_{46}H_{32}O_{15}$ Acetyl derivative of hydroxyquinol-benzein (GHOSH and WATSON), P., 10.

$C_{46}H_{70}O_8$ Diacetylcaulosapogenin, and its sodium salt (POWER and SALWAY), T., 199.

 C_{47} Group.

$C_{47}H_{52}N_6$ 1:2:3-Trisdiethylaminoanilo-4:5-diphenyl- $\Delta^{4:5}$ -cyclopentene (RUHEMANN and LEVY), T., 561.

C₄₈ Group.

- C₄₈H₄₂O₅Si₄** Trianhydrotetrakis(diphenylsilicanediol (KIPPING and ROBINSON), P., 375.
C₄₈H₉₃O₉N Cerebrone, isolation and purification of (LAPWORTH), T., 1029; P., 175.

C₅₀ Group.

- C₅₀H₆₀O₁₀** Tetra benzoylhexadecyl-*d*-glucoside (SALWAY), T., 1029.
C₅₀H₇₄O₁₀ Tetra-acetylcaulosapogenin (POWER and SALWAY), T., 199.
C₅₀H₇₆O₇ Substance, from oleanone and dilute acetic acid (TUTIN and NAUNTON), T., 2057; P., 301.

C₅₂ Group.

- C₅₂H₈₀O₈** Acetyl derivative of substance **C₅₀H₇₈O₇** (TUTIN and NAUNTON), T., 2057; P., 301.

C₅₄ Group.

- C₅₄H₈₂O₉** Diacetyl derivative of substance **C₅₀H₇₈O₇** (TUTIN and NAUNTON), T., 2057.
C₅₄H₈₈O₁₇ Caulosaponin (+4H₂O) (POWER and SALWAY), T., 198; P., 2.

C₅₆ Group.

- C₅₆H₈₈O₉** Caulophyllosapogenin (POWER and SALWAY), T., 205; P., 2.

C₅₈ Group.

- C₅₈H₉₂O₉** Caulophyllosapogenin dimethyl ether (POWER and SALWAY), T., 206.

C₆₁ Group.

- C₆₁H₇₂O₁₀** Tetrabenzoylsitosterol-*d*-glucoside (SALWAY), T., 1025.

C₆₆ Group.

- C₆₆H₁₀₂O₇** Substance, from heating diacetyloleanol (TUTIN and NAUNTON), T., 2054.
C₆₆H₁₀₄O₁₇ Caulophyllosaponin (POWER and SALWAY), T., 204; P., 2.

C₆₈ Group.

- C₆₈H₁₀₀O₁₅** Hexa-acetylcaulophyllosapogenin (POWER and SALWAY), T., 205.

C₇₀ Group.

- C₇₀H₈₂O₁₀** Tetrabenzoylcaulosapogenin (POWER and SALWAY), T., 200.

C₇₄ Group.

- C₇₄H₁₀₈O₂₇** Deca-acetylcaulosaponin (POWER and SALWAY), T., 198.

C₈₄ Group.

- C₈₄H₈₆Br₂** Substance, from 2:2'-dibromodiphenyl and sodium (DOBBIE, Fox, and GAUGE), T., 38.

C₈₆ Group.

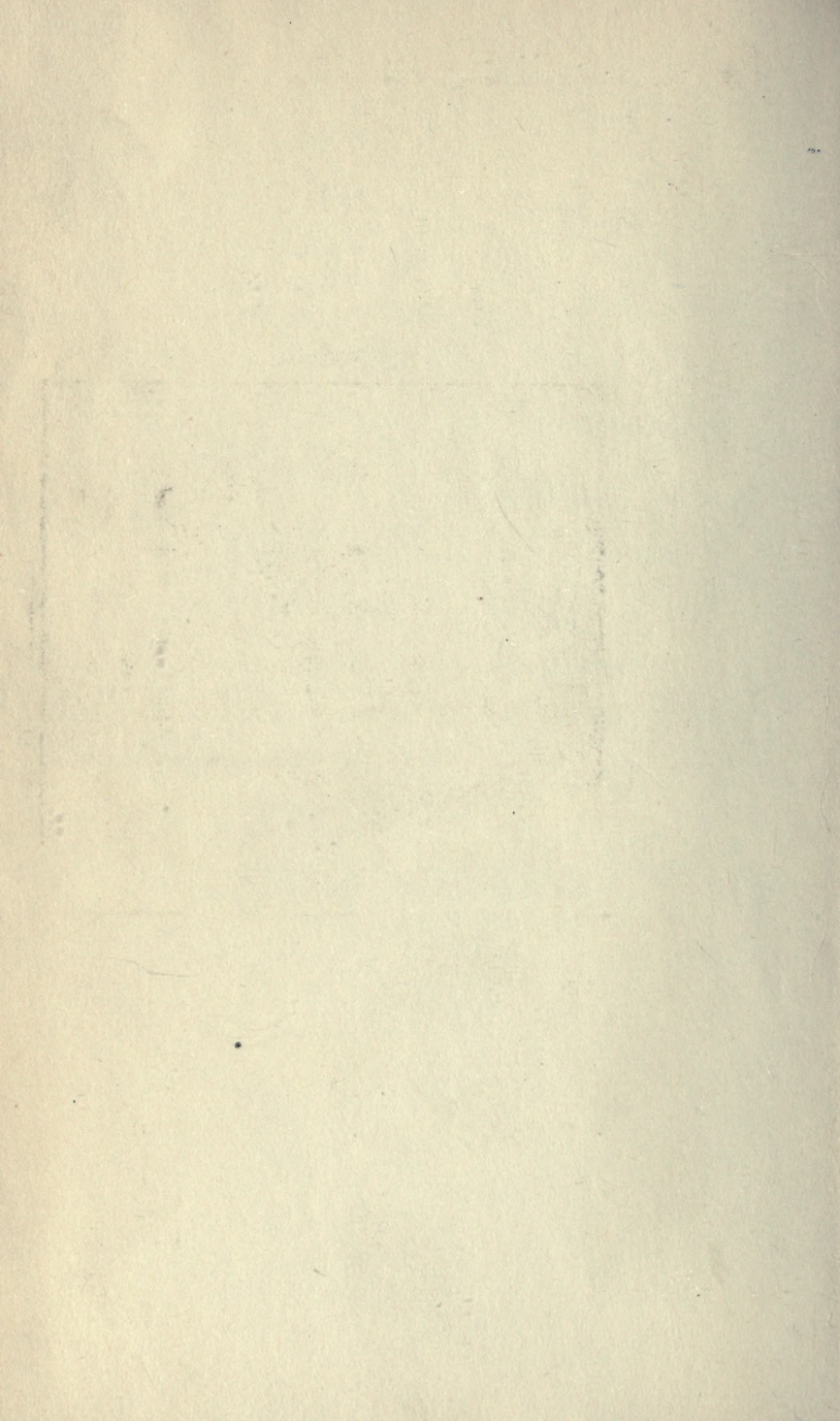
- C₈₆H₁₂₄O₂₇** Deca-acetylcaulophyllosaponin (POWER and SALWAY), T., 204.
 2359.

ERRATA.

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Page	Line	
153	27	for "ethyl di- <i>p</i> -toluoyl." read "ethyl di- <i>p</i> -nitrobenzoyl-."
165	1	asterisk refers to footnote on p. 164.
611	16-17	for "whence $[\alpha]_D + 7.21^\circ$ and $[M]_D + 22.9^\circ$ " read "whence $[\alpha]_D + 3.72^\circ$ and $[M]_D + 11.8^\circ$."
638	Fig. 1	Ordinates: for "1.200" and "1.400" read "1.02" and "1.04" (upper curve should accordingly be much steeper).
947		in formula II for $\begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array}$ read $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array}$
	Line	
1565	19	for "bromobenzene" read "bromonaphthalene."
1571	20	„ "derived" read "derivative."
1582	5	„ " $\text{C}_{14}\text{H}_{14}\text{O}_{12}\text{Ba}_3$ " read " $\text{C}_{14}\text{H}_{14}\text{O}_{12}\text{Ba}_3, 4\text{H}_2\text{O}$."
1588	7* and 26* }	in equation omit "+ H_2O ."
1613	16*	for $\begin{array}{c} \text{C}_6\text{H}_5\cdot\text{C} \\ \parallel \\ \text{N}\cdot\text{OH} \end{array}$ read $\begin{array}{c} \text{C}_6\text{H}_5\cdot\text{CH} \\ \parallel \\ \text{N}\cdot\text{OH} \end{array}$
1624	6	„ "tube to 100°" „ "tube with benzene to 100°."
1852	13	„ " $\text{C}_{15}\text{H}_9\text{O}_3\text{N}_2$ " „ " $\text{C}_{15}\text{H}_9\text{O}_3\text{N}_2\text{Na}$."
1928	1*	„ "marked" „ "masked."
2301	2* }	
2311	29* }	„ "Willsdon" „ "Willson."

* From bottom.



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